

ANALYTIC ONE-ELECTRON RESPONSE PROPERTIES,
MOLECULAR GRADIENTS, AND FORCE CONSTANTS
IN MANY-BODY METHODS

By

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To Mom, Dad and Susy

To all the Boys in the Clubhouse

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The theory of analytic first and second derivatives of the Coupled-Cluster (CC) energy is presented. First derivatives of the energy, corresponding to first-order one-electron response properties and molecular gradients, are expressed in terms of the response (or "relaxed") density for efficient evaluation. Explicit expressions for the derivative energy and response density for the Coupled-Cluster Singles, Doubles and Triples (CCSDT) model are presented; expressions for the finite-order Many-Body Perturbation Theory (MBPT) models through full fourth order are extracted from low-order iterations of the derivative CCSDT expressions.

Second derivatives of the CC energy, corresponding to second-order one-electron response properties and force constants, are expressed in terms of the response density and first-derivative CC t-amplitudes. Explicit expressions for the second derivative of the energy are presented for the CCSDT-1 model, the CCSDT model truncated to linear

triple-excitation contributions. Expressions for the second derivative of the finite-order MBPT energies through full fourth order are presented as well.

BACKGROUND: MODELS FOR CORRELATION

Many of the traditional tools for approximating eigenfunctions and eigenvalues of the electronic Hamiltonian are based upon the variational principle. Given the choice of an atomic orbital basis set, which usually consists of Gaussian functions centered upon the nuclei in the molecular system, the Self-Consistent Field (SCF) method is commonly applied. The SCF procedure determines a set of molecular orbitals, one-electron functions of space and spin, as linear combinations of the atomic orbital basis functions. The SCF wavefunction is an antisymmetrized product (Slater determinant) of the occupied molecular orbitals; the SCF electronic energy is the expectation value of the electronic Hamiltonian over the SCF wavefunction. The SCF molecular orbital coefficients are variationally optimal for a single-determinant description of the electronic wavefunction. In the SCF model, each electron moves in an effective potential--an average of its interactions with all other electrons in the system, plus its coulomb attraction for the nuclei. The SCF method is inexpensive but not very accurate in its prediction of molecular structure and properties. Consequently, there exist "correlated" methods which restore the true electronic interactions by going beyond the single-determinant description of the electronic wavefunction and the effective SCF Hamiltonian.

As a by-product of the SCF method, molecular orbitals of two types are determined: the "occupied" orbitals and the "virtual" (or

"unoccupied") orbitals. The virtual SCF orbitals, in conjunction with the SCF determinant, are used to define "excited" determinants. The collection of all determinants obtained by replacing one occupied orbital in the SCF determinant with a virtual orbital compose the singly-excited determinants. The collection of determinants where two occupied orbitals have been replaced by two virtual orbitals compose the doubly-excited determinants. Triple and higher excitations are analogously defined. The Configuration Interaction (CI) method refers to the construction and subsequent diagonalization of the matrix representation of the Hamiltonian in the basis of all such determinants. The CI electronic wavefunction is then the SCF determinant plus a linear combination of excited determinants. Furthermore, the CI wavefunction is variationally the best possible wavefunction in the basis set spanned by the determinants, and by definition, is "fully correlated."

For practical purposes, the full CI problem is not tractable because the complete set of excited determinants is usually extremely large. Indeed, if the number of atomic basis functions (M) is large, there are approximately $M!$ excited determinants. The basis set of the Hamiltonian is therefore truncated to include only excited determinants of certain types. For example, simple models might contain doubly-excited determinants (CID) or singly- and doubly-excited determinants (CISD). The lowest eigenvalue and corresponding eigenvector are extracted from the truncated CI Hamiltonian matrix, yielding a wavefunction that is variationally the best wavefunction in the truncated space.

Alternatively, the deficiencies of the SCF wavefunction and SCF effective Hamiltonian are circumvented by the Multi-Configuration SCF

(MCSCF) method. Like the truncated CI wavefunction, the MCSCF wavefunction is a linear-combination of a selected set of determinants, where the coefficients are variationally optimal. Unlike the CI method, however, the orbitals are not fixed by the SCF method but are allowed to vary as well.

Many-body methods such as the Coupled-Cluster (CC) method and Many-Body Perturbation Theory (MBPT) are often the modern methods of choice for solving the correlation problem. Although many-body methods are not variational, they provide accurate approximations to the full CI wavefunction and full CI energy eigenvalue and possess the size-extensive property of the full CI model. A model is said to be size-extensive if the energy scales properly with the size of the molecule. Consider, for example, a system composed of N identical, non-interacting components. The full CI energy of the system will necessarily be N times the energy of a single component. The approximate many-body energy of the system will also be N times the approximate many-body energy of a single component. Chemical systems are understood at the most fundamental level of approximation to be composed largely of independent electron pairs; thus, the errors of truncated CI or MCSCF approximations, which do not preserve the size-extensive property, can be quite large.

INTRODUCTION

The evaluation of energy derivatives is a necessary element of the ab initio prediction of molecular structure and properties. Derivatives of the energy with respect to nuclear displacement parameters, called "molecular gradients", represent the forces acting on the nuclei and are necessary input for search algorithms which locate critical points on a molecule's potential energy surface. Once a critical point has been found, the second derivatives of the energy, evaluated perhaps by finite-difference of analytic molecular gradients, characterize the point as a minimum (a stable molecular structure) or a saddle point (a transition state) or neither. Second derivatives of the energy make possible the prediction of harmonic vibrational frequencies and intensities, as well. Derivatives of the energy with respect to external field perturbation parameters are directly associated with the one-electron response properties of the molecule. The prediction of molecular structure and properties using highly correlated many-body methods have become standard in quantum chemical studies; in this work, procedures for the efficient evaluation of analytic first derivatives of the MBPT/CC energy are presented.

One-electron response properties are often computed in the framework of approximate CI models as derivatives rather than as expectation values. In the full CI model, the derivative approach yields the same result as an expectation value; a Hellman-Feynman

Theorem is said to exist for the full CI wavefunction. The Hellman-Feynman Theorem applies to the SCF model, too. For many approximate models of correlation, however, the expectation value and derivative are not the same. In fact, the derivative is the expectation value plus additional terms which usually bring the derivative closer to the full CI property value. First-order response properties in the MBPT/CC model are shown to be simple dot-products between the response or "relaxed" MBPT/CC density matrix and the one-electron perturbation matrix of interest.

Molecular gradients are treated as special cases of a response property, wherein the basis functions are dependent upon the nuclear displacement perturbation. The Gaussian basis functions are fixed to the nuclei, and when the nuclei move, the basis functions move as well. In addition to the response-property term, there are terms involving the derivative of the atomic orbital basis functions in two-electron integrals and in overlap integrals.

The evaluation of energy derivatives of variational methods can be simplified in ways, which, in general, the evaluation of energy derivatives of many-body methods cannot. The energy is generally a function of the molecular orbital coefficients c , the coefficients in the determinantal expansion of the wavefunction C , and the one- and two-electron integrals (I) involving the atomic orbital basis set functions. The derivative of the energy is in general:

$$\frac{\partial E(c(X), C(X), I(X))}{\partial X} = \frac{\partial E}{\partial c} \frac{\partial c}{\partial X} + \frac{\partial E}{\partial C} \frac{\partial C}{\partial X} + \frac{\partial E}{\partial I} \frac{\partial I}{\partial X}.$$

In the case of the SCF model, the wavefunction is a single determinant and the energy is optimal with respect to changes in the molecular

orbital coefficients; that is, $\partial E/\partial c = 0$. It is not necessary to evaluate $\partial c/\partial \chi$, the derivative of the molecular orbital coefficients with respect to the perturbation parameter. If χ represents a nuclear displacement parameter, the third term indicates that it is necessary to evaluate $\partial E/\partial I$, how the SCF energy varies relative to the one- and two-electron integrals, and in turn to evaluate $\partial I/\partial \chi$, how the integrals vary relative to the nuclear displacement parameter. Such contributions distinguish the Generalized Hellman-Feynman Theorem from the ordinary Hellman-Feynman Theorem. Similarly, in the case of the MCSCF model, we have $\partial E/\partial C = 0$ and $\partial E/\partial c = 0$, and again only the third term remains. In CI methods, the energy is optimal with respect to the determinantal coefficients only; that is, we have $\partial E/\partial C = 0$ and $\partial E/\partial c \neq 0$.

In the Coupled-Cluster method¹⁻¹¹ and its finite-order MBPT approximations,^{3,5,8,12-14} the energy is not optimal with respect to the molecular orbital coefficients or the determinantal coefficients. It is necessary to take into account the derivative of the CC energy with respect to the SCF coefficients and with respect to the determinantal coefficients, and in turn, the derivative of the SCF coefficients and the determinantal coefficients with respect to the perturbation parameter. It might appear that for the evaluation of several properties and/or the $3N$ molecular gradients (for a system of N nuclei), it is necessary to evaluate $\partial C/\partial \chi$ and $\partial c/\partial \chi$ for each perturbation of interest. However, the equation governing the response of the SCF coefficients is a linear equation, as is the equation governing the response of the CC determinantal coefficients. Consequently, the first and second terms of the energy derivative expression can be transformed into a computationally efficient form.

The determinantal coefficient derivatives for each perturbation need not be determined; only a single, perturbation-independent linear equation must be solved. Analogously, the SCF coefficient derivatives for each perturbation need not be determined; once again, it is necessary to solve only a single, perturbation-independent linear equation in order to evaluate the energy derivative. A special property, the response or "relaxed" density, emerges naturally from the transformation to perturbation-independent expressions.

Analytic gradients for the SCF,¹⁵ MCSCF,¹⁶ CI,¹⁷ and MBPT(2)¹⁸ models have been available for some time. Recent developments in the analytic evaluation of CC/MBPT gradients have been based upon perturbed CC theory.¹⁹⁻²² The first reports of the theory and application of MBPT(3), D-MBPT(4) and CCD gradients^{23,24} were not suitable for routine applications since they did not take advantage of the linear nature of the CC derivative equations. The general theory of CC derivatives was later presented in an efficient form,^{25,26} and analytic CCSD gradients were subsequently reported.²⁷ Analytic SDQ-MBPT(4) gradients have been recently reported,²⁸ but the implementation did not take advantage of the linear nature of the SCF derivative equations. The most recent gradient work^{27,28} has incorporated the discussion of Handy et al.²⁹ on the elimination of singularities which arise when there are degenerate or near-degenerate orbital eigenvalues.

Since the equations governing the second-order response of the SCF coefficients and the CC determinantal coefficients are linear, there is no need to solve explicitly for second derivative SCF coefficients or second derivative determinantal coefficients in order to evaluate a CC second derivative. In simplest form, second derivatives of the CC

energy are expressed in terms of the relaxed density and first-derivative CC t-amplitudes.

The evaluation of second derivatives at the SCF level of theory¹⁸ is commonplace today; the theory and application of analytic many-body second derivatives is currently limited to the simplest model--second order perturbation theory.^{29,30}

In this work, the CCSDT derivative energy expressions are derived using diagrammatic rules developed for second-quantized operators. The finite-order MBPT derivative models through full fourth order are obtained by iteration of the CC derivative equations. The theory of CC/MBPT second derivatives is presented. Explicit expressions for the second derivative of the energy are presented for the CCSDT-1 model, the CCSDT model truncated to linear triple-excitation contributions. Second derivative expressions for the finite-order MBPT models through full fourth order are provided as well.

THE COUPLED-CLUSTER MODEL

Consider the Schrödinger Equation corresponding to a molecular system, where the electronic Hamiltonian $H(X)$, its eigenfunction $\Psi(X)$, and its eigenvalue $E(X)$ are dependent upon some parameter X :

$$H(X) \Psi(X) = E(X) \Psi(X) \quad (1)$$

$$H(X) = -1/2 \sum_i \nabla_i^2 - \sum_{i,\alpha} Z_\alpha \frac{1}{r_{\alpha i}} + \sum_i X Q_i + \sum_{i>j} r_{ij}^{-1} .$$

The parameter may control the displacement of an atomic nucleus in the molecular system, or it may be the strength of an external one-electron potential energy perturbation Q_i , such as a uniform electric field applied in the z -direction: $X Q_i = X z_i$. The one-body part of the electronic Hamiltonian is composed of three parts: the kinetic energy operators of the electrons; the potential energy operators of the electrons due to the nuclei present; and a potential energy operator due to an externally applied field, if present. The two-body operator is the electron-electron repulsion operator. Here, the labels i and j represent the electrons in the system; the label α represents the nuclei, and Z_α is the charge of nucleus α . In correlated methods, we seek the solution to Equation (1) in the space of the N -electron determinants (antisymmetrized products) formed from a basis of orthonormal one-electron spin-orbitals $\{\phi(X)\}$. The solution is built upon an approximate single-determinant wavefunction, called the

reference function and denoted by $|0\rangle$. The total energy of the molecular system, within the Born-Oppenheimer or "fixed nuclei" approximation, is obtained by adding the nuclear repulsion energy to the electronic energy $E(X)$.

The reference energy is defined as the expectation value of the Hamiltonian over the reference wavefunction $\langle 0|H(X)|0\rangle$. Subtraction of the reference energy from each side of Equation (1) yields:

$$\begin{aligned} (H(X) - \langle 0|H(X)|0\rangle) \Psi(X) &= (E(X) - \langle 0|H(X)|0\rangle) \Psi(X) \\ \text{or} \quad H_N(X) \Psi(X) &= \Delta E(X) \Psi(X) \quad (2) \end{aligned}$$

$H_N(X)$ is the "normal product" form of the Hamiltonian and is represented in terms of the second-quantized operators by:

$$H_N(X) = \sum_{p,q} \left(h_{pq} + \sum_i \langle pi||qi \rangle \right) \{p^+q\} + \frac{1}{4} \sum_{\substack{p,q, \\ r,s}} \langle pq||rs \rangle \{p^+q^+sr\} \quad (3)$$

By convention, the indices i,j,k,l,\dots represent the spin orbitals which are occupied in the reference function $|0\rangle$. The indices a,b,c,d,\dots correspond to the virtual (or unoccupied) spin orbitals. The indices p,q,r,s,\dots are unrestricted.

The symbols h_{pq} and $\langle pq||rs \rangle$ in Equation (3) represent integrals wherein the one- and two-electron operators of the Hamiltonian act upon the orbital basis functions:

$$h_{pq} = \int \phi_p^*(1) \left(-1/2 \nabla_1^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{\alpha 1}} + \chi Q_1 \right) \phi_q(1) \partial \tau_1 \partial \sigma_1$$

$$\langle pq || rs \rangle = \iint \phi_p^*(1) \phi_q^*(2) \left(r_{12}^{-1} - P_{12} \right) \phi_r(1) \phi_s(2) \partial \tau_1 \partial \sigma_1 \partial \tau_2 \partial \sigma_2 \quad .$$

The variables σ_1 and τ_1 are the coordinates of spin and space of electron number one, respectively. The operator P_{12} is the permutation operator; thus the integral $\langle pq || rs \rangle$ is antisymmetric with respect to the exchange of p with q or r with s . The integral h_{pq} is explicitly dependent upon χ if a one-electron potential energy perturbation Q_1 is present. Of course, if the perturbation is a nuclear displacement, the h_{pq} integrals depend upon χ through the operator $Z_\alpha / r_{\alpha 1}$ as well. In general, both h_{pq} and $\langle pq || rs \rangle$ are implicitly dependent upon χ through the orbital basis functions, since the basis functions vary with molecular geometry or external field strength. Consider the common choice of SCF molecular orbitals as the orbital basis. Self-Consistent Field orbitals are determined in the presence of the effective Fock potential which contains the entire one-electron part of the Hamiltonian. In addition, the SCF molecular orbitals are determined as linear combinations of primitive AO basis functions, and if the perturbation is a nuclear displacement, the primitive AO basis functions centered upon that nucleus are displaced as well.

The operators p^+ and q are the second-quantized creation and annihilation operators, respectively. Excited determinants are represented in second-quantization by a string of creation and annihilation operators acting on the reference function, whereby an electron in an occupied orbital is "annihilated" and an electron is subsequently "created" in a virtual orbital:

$$\{a^+i\}|0\rangle = |S\rangle \quad \text{Singly-excited determinant}$$

$$\{a^+ib^+j\}|0\rangle = |D\rangle \quad \text{Doubly-excited determinant}$$

$$\{a^+ib^+jc^+k\}|0\rangle = |T\rangle \quad \text{Triply-excited determinant}$$

.
.
.

etc.

Brackets enclosing a second-quantized operator string {ABCD...} denote a normal product of operators. The normal product of a second-quantized operator string is defined by moving all a, b, \dots and i^+, j^+, \dots operators to the right of the operator string by use of the anticommutation relations which govern second-quantized operators:

$$[a^+, b]_+ = \delta_{ab} \quad \text{and} \quad [i^+, j]_+ = \delta_{ij} \quad .$$

The anticommutation relations follow from the defining conditions: $a|0\rangle = i^+|0\rangle = 0$. The normal-ordered form of the Hamiltonian³¹ in Equation (3) is obtained by application of Wick's Theorem to the ordinary second-quantized Hamiltonian. Wick's Theorem states that a string of m second-quantized operators ABCD... equals the normal product of the string plus all possible one-fold, two-fold, ..., up to m -fold contracted normal products of the string.³¹

$$\begin{aligned}
ABCD\dots &= \{ABCD\dots\} + \{\overline{AB}CD\dots\} + \{\overline{A}B\overline{C}D\dots\} + \{\overline{A}B\overline{C}D\dots\} + \{\overline{A}B\overline{C}D\dots\} \\
&\quad + \text{(all other one-fold contracted products)} \\
&\quad + \{\overline{AB}\overline{C}D\dots\} + \{\overline{A}B\overline{C}D\dots\} + \{\overline{A}B\overline{C}D\dots\} + \{\overline{A}B\overline{C}D\dots\} \\
&\quad + \text{(all other two-fold contracted products)} \\
&\quad \vdots \\
&\quad + \text{(all m-fold contracted products)}
\end{aligned}$$

A contraction between operators A and B is defined as

$$\overline{AB} = AB - \{AB\}.$$

The only nonvanishing contractions are

$$\overline{i^+j} = \delta_{ij} \quad \text{and} \quad \overline{ab^+} = \delta_{ab}.$$

It follows that all contractions of a normal product of operators $\{ABCD\dots\}$ are vanishing ones. The expectation value of a second-quantized operator string over the reference (or Fermi vacuum) can be evaluated by forming all of the fully contracted products.

$$\langle 0|ABCD\dots|0\rangle = \text{(all m-fold contracted products)}$$

So, the expectation value of a normal product over the reference is zero.

$$\langle 0|\{ABCD\dots\}|0\rangle = 0$$

The Generalized Wick's Theorem³¹ states that a product of operator strings in which some operator strings are already in normal product form is given as the normal product of the overall string plus the sum of all possible normal products with contractions; however, no contractions between pairs of operators within an original normal product are included. A corollary is that for the expectation value of a product of normal product operators over the reference (or Fermi vacuum), only the fully contracted products are non-zero.

The representation of the Fock operator in the orbital basis is given by the matrix elements

$$f_{pq} = h_{pq} + \sum_i \langle pi || qi \rangle .$$

So we may represent $H_N(X)$ as

$$H_N(X) = \sum_{p,q} f_{pq} \{p^+q\} + \frac{1}{4} \sum_{\substack{p,q, \\ r,s}} \langle pq || rs \rangle \{p^+q^+sr\} \quad (4)$$

$$\text{or} \quad H_N(X) = f_N(X) + W_N(X) .$$

If the SCF wavefunction is chosen as the reference function, $\langle 0 | H(X) | 0 \rangle$ is the SCF energy, $\Delta E(X)$ is the correlation energy, and the Hamiltonian simplifies to

$$H_N(X) = \sum_{i,j} f_{ij} \{i^+j\} + \sum_{a,b} f_{ab} \{a^+b\} + \frac{1}{4} \sum_{\substack{p,q, \\ r,s}} \langle pq || rs \rangle \{p^+q^+sr\} ,$$

since the matrix elements f_{ai} and f_{ia} are zero for SCF orbitals. For the particular choice of canonical SCF orbitals, we have, by definition, $f_{ij} = \delta_{ij}\epsilon_i$ and $f_{ab} = \delta_{ab}\epsilon_a$, where ϵ_p denotes the molecular orbital eigenvalue of orbital p .

The CC method¹⁻¹¹ proceeds by choosing an exponential form of $\Psi(X)$. That is,

$$\Psi(X) = e^{T(X)}|0\rangle, \quad (5)$$

where $T(X)$ is a sum of excitation operators

$$T(X) = T_1(X) + T_2(X) + T_3(X) + \dots$$

The excitation operators are given by

$$\begin{aligned} T_1(X) &= \sum_{i,a} t_i^a(X) \{a^+i\} \\ T_2(X) &= \frac{1}{4} \sum_{i,j} \sum_{a,b} t_{ij}^{ab}(X) \{a^+ib^+j\} \\ &\vdots \\ T_n(X) &= \frac{1}{(n!)^2} \sum_{i,j,\dots} \sum_{a,b,\dots} t_{ij\dots}^{ab\dots}(X) \{a^+ib^+j\dots\} \\ &\vdots \end{aligned}$$

where the t -amplitudes are to be determined.

Substitution of Equation (5) into Equation (2) yields:

$$H_N(X) e^{T(X)} |0\rangle = \Delta E(X) e^{T(X)} |0\rangle$$

$$\text{or} \quad e^{-T(X)} H_N(X) e^{T(X)} |0\rangle = \Delta E(X) |0\rangle. \quad (6)$$

The Hausdorff expansion of $e^{-A} B e^A$ yields a series of commutators:

$$e^{-A} B e^A = B - [A, B] + \frac{1}{2!} [A, [A, B]] - \frac{1}{3!} [A, [A, [A, B]]] + \dots$$

Since a product of normal product operators can be written as a sum of contracted terms, it follows that a product AB has a "connected" part and a "disconnected" part. In the connected part there is at least one contraction that connects A to B ; in the disconnected part there is no such contraction. For a commutator of operators $[A, B]$, the disconnected parts cancel, leaving only the connected parts:

$$[A, B] = AB - BA = (AB)_c - (BA)_c + (AB)_d - (BA)_d = [A, B]_c.$$

Thus the expansion becomes

$$e^{-A} B e^A = B - [A, B]_c + \frac{1}{2!} [A, [A, B]_c]_c - \frac{1}{3!} [A, [A, [A, B]_c]_c]_c + \dots$$

Furthermore, if A is an excitation operator, A cannot give rise to a connected contribution when it is to the left of other operators.

Consequently, the expansion reduces to the following form:

$$\begin{aligned}
e^{-A} B e^A &= B + (BA)_c + \frac{1}{2!} ((BA)_c A)_c + \frac{1}{3!} (((BA)_c A)_c A)_c + \dots \\
&= (Be^A)_c .
\end{aligned}$$

So Equation (6) can be represented as

$$(H_N(X) e^{T(X)})_c |0\rangle = \Delta E(X) |0\rangle . \quad (7)$$

By projecting Equation (7) on the left by $\langle 0|$, we obtain the CC energy expression:

$$\Delta E(X) = \langle 0| (H_N(X) e^{T(X)})_c |0\rangle . \quad (8)$$

The t-amplitudes are determined by solving the set of coupled equations obtained by projection of the singly-, doubly-, triply- ... excited determinants (S, D, T, ...):

$$\langle S| (H_N(X) e^{T(X)})_c |0\rangle = 0 \quad (9)$$

$$\langle D| (H_N(X) e^{T(X)})_c |0\rangle = 0$$

$$\langle T| (H_N(X) e^{T(X)})_c |0\rangle = 0$$

$$\vdots$$

Various CC models result from choices of truncation of $T(X)$. For example, the CCD model is defined by the choice $T(X) = T_2(X)$, the CCSD model is defined by $T(X) = T_1(X) + T_2(X)$ and the CCSDT model is defined by $T(X) = T_1(X) + T_2(X) + T_3(X)$. In the limit of including

all excitation operators in $T(X)$, the full CI wavefunction and energy is recovered.

Diagrammatic rules³² are used to identify all of the fully contracted products in the CC amplitude equations and energy expression; the diagrams are then interpreted algebraically. The operators $f_N(X)$ and $W_N(X)$, which compose the normal product Hamiltonian $H_N(X)$, are represented diagrammatically in Figure (1). The CC excitation operators $T_1(X)$, $T_2(X)$, and $T_3(X)$ are represented by the diagrams in Figure (2). The diagrams representing each of the fully contracted products in the CC energy expression is shown in Figure (3). The diagrammatic equations for the $T_1(X)$, $T_2(X)$ and $T_3(X)$ amplitudes are shown in Figures (4), (5), and (6), respectively. In the diagrams, the operator diagrams from $H_N(X)$ and $e^{T(X)}$ are connected together; each connection represents a contraction between the operators. A diagram's excitation level--the number of pairs of unconnected lines at the top of the diagram, matches the excitation level of the projected determinant. That is, all diagrams in the energy expression, obtained by left-projection of $\langle 0|$, have a zero excitation level. The diagrams in the $T_1(X)$ equation, obtained by left-projection of $|S\rangle$ have an excitation level of one. The $T_2(X)$ equation consists of diagrams of excitation level two, and so forth. The explicit algebraic expressions for the CCSDT model are presented elsewhere.¹⁰

For the choice of canonical SCF orbitals as the orbital basis, the terms involving the $f_N(X)$ operator simplify because f_{pq} is zero except along the diagonal where the orbital eigenvalues are. Consider an iterative form of the equations where the diagrams (3a,b) in Figure (4) are taken to the other side of the $T_1(X)$ equation, diagrams (2a,b)

in Figure (5) are taken to the other side of the $T_2(X)$ equation, and diagrams (3a,b) in Figure (6) are taken to the other side of the $T_3(X)$ equation. Solutions to the equations may be constructed by forming successive iterates of increasing order in the correlation perturbation $W_N(X)$. Iteration of the amplitude equations and subsequent substitution into the energy expression yield the finite-order MBPT energies. Attention is centered upon the $T_2(X)$ amplitudes, since through fourth-order MBPT, only the $T_2(X)$ amplitudes contribute directly to the correlation energy by way of the third diagram in Figure (3).

The first-order iterate of $T_2(X)$ arises from the constant term in the $T_2(X)$ equation represented by diagram (1) in Figure (5). The amplitudes are obtained by dividing the constant term by the eigenvalues derived from the diagrams (2a,b), mentioned above. Substitution into the energy expression yields the second-order energy MBPT(2). MBPT diagrams are described in terms of the order of the correlation perturbation $W_N(X)$ and in terms of the excitation level of the determinant from which the energy contribution arises. The SCF energy is complete through first order in $W_N(X)$; thus the MBPT correlation models begin at second order in $W_N(X)$. The MBPT(2) energy is represented by a single MBPT diagram, and it originates from doubly-excited determinants in the correlated wavefunction.

The second-order iterate of $T_2(X)$ arises from the substitution of the first-order iterate into the linear terms of the $T_2(X)$ equation—diagrams (2c-e) in Figure (5). The second-order iterate is completed by dividing through by the eigenvalues derived from the diagram (2a,b). Substitution of the second-order iterate of $T_2(X)$ into the

energy expression yields the three diagrams of the MBPT(3) model, all arising from doubly-excited determinants, as well.

The third-order iterate of $T_2(X)$ has contributions from four sources: the lowest-order iterate of $T_1(X)$, which happens to be second order in $W_N(X)$, contributes to $T_2(X)$ by way of diagrams (3a,b) in Figure (5); the second-order iterate of $T_2(X)$ contributes to $T_2(X)$ through the linear diagrams (2c-e) of Figure (5); the lowest-order iterate of $T_3(X)$, which also happens to be second-order in $W_N(X)$, contributes to $T_2(X)$ by way of diagrams (4b,c) in Figure (5); the first-order iterate contributes to $T_2(X)$ by way of the quadratic part of the $T_2(X)$ equation--diagrams (5a-d) in Figure (5). The result of substitution of the third-order $T_2(X)$ iterate into the energy expression is that corresponding fourth-order MBPT energy contributions: S(4), D(4), T(4) and Q(4).³³ The letters S, D, T and Q indicate that the contributions are generated by single, double, triple and quadruple excitations, respectively. The lowest-order iterate of $T_1(X)$ is obtained by substitution of the first-order iterate of $T_2(X)$ into diagrams (2b,c) in Figure (4) and subsequently dividing by the eigenvalues derived from diagrams (3a,b). The lowest-order iterate of $T_3(X)$ is obtained by substitution of the first-order iterate of $T_2(X)$ into diagrams (1a,b) in Figure (6), and subsequently dividing by the eigenvalues derived from diagrams (3a,b). Finally, we note that the quadratic part of the $T_2(X)$ equation, giving rise to the Q(4) MBPT energy diagrams, has its origins in the $T_2(X)^2$ part of the exponential wavefunction; the lowest-order energy contributions from quadruply-excited determinants are actually products of doubly-excited determinants.

For practical molecular systems, computational limitations often force the restriction to a partial inclusion of $T_3(X)$ in the CC equations. The CCSDT-1 model is defined by truncation of the $T_3(X)$ amplitude equation to diagrams (1a,b) in Figure (6) and by the restriction of $T_3(X)$ contributions to $T_1(X)$ and $T_2(X)$ to the linear terms. That is, $T_3(X)$ is permitted to contribute to $T_1(X)$ only through diagram (4) in Figure (4) and to contribute to $T_2(X)$ only through diagrams (4a-c) in Figure (5). The lowest-order $T_3(X)$ approximation is preserved so that the CCSDT-1 model is complete through the fourth-order MBPT energy and the second-order MBPT wavefunction.

Because the equations for the CC amplitudes are connected, the subsequent substitution of the amplitudes into the energy expression, which is connected and closed, yields only "linked" energy diagrams. That is, no diagram has a closed, disconnected part. The size-extensive property⁸ of the CC/MBPT models follows from the fact that all energy contributions are linked.

The choice of a particular CC or MBPT model defines an approximate solution to Equation (2). The approximate total energy of the molecular system is obtained by adding the nuclear repulsion energy and reference energy to the approximate ΔE^X . In the absence of analytic methods, the derivative of the total energy at $X=0$ is computed by finite difference of the total energy evaluated at a small positive and a small negative value of X . In the next section, we will obtain analytical expressions for the evaluation of $(\partial \Delta E / \partial X)|_{X=0}$, so that together with analytic derivatives of the reference energy and the nuclear repulsion energy, we will have the analytic derivative of the total energy.

$$f_{pq} \{ p^\dagger q \} = \begin{array}{c} \downarrow \nearrow \\ \text{---} x \end{array} + \begin{array}{c} \uparrow \\ \text{---} x \\ \downarrow \end{array} + \begin{array}{c} \downarrow \\ \text{---} x \\ \uparrow \end{array} + \begin{array}{c} \downarrow \nearrow \\ \text{---} x \end{array}$$

$$\begin{aligned} \langle pq || rs \rangle \{ p^\dagger q^\dagger sr \} = & \begin{array}{c} \downarrow \nearrow \downarrow \nearrow \\ \text{---} \end{array} + \begin{array}{c} \downarrow \nearrow \\ \text{---} \end{array} \begin{array}{c} \downarrow \nearrow \\ \text{---} \end{array} + \begin{array}{c} \uparrow \\ \text{---} \end{array} \begin{array}{c} \uparrow \\ \text{---} \end{array} \begin{array}{c} \downarrow \nearrow \\ \text{---} \end{array} + \begin{array}{c} \downarrow \nearrow \\ \text{---} \end{array} \begin{array}{c} \downarrow \nearrow \\ \text{---} \end{array} + \begin{array}{c} \downarrow \nearrow \downarrow \nearrow \\ \text{---} \end{array} \\ & + \begin{array}{c} \uparrow \\ \text{---} \end{array} \begin{array}{c} \downarrow \nearrow \\ \text{---} \end{array} + \begin{array}{c} \uparrow \\ \text{---} \end{array} \begin{array}{c} \uparrow \\ \text{---} \end{array} \begin{array}{c} \uparrow \\ \text{---} \end{array} + \begin{array}{c} \downarrow \nearrow \\ \text{---} \end{array} \begin{array}{c} \downarrow \nearrow \\ \text{---} \end{array} + \begin{array}{c} \uparrow \\ \text{---} \end{array} \begin{array}{c} \downarrow \nearrow \\ \text{---} \end{array} \end{aligned}$$

Figure 1. The Diagrammatic Representation of $H_N(X)$.

$$t_i^a \{ a^\dagger i \} = \begin{array}{c} \downarrow \nearrow \\ \text{---} \end{array}$$

$$t_{ij}^{ab} \{ a^\dagger i b^\dagger j \} = \begin{array}{c} \downarrow \nearrow \downarrow \nearrow \\ \text{---} \end{array}$$

$$t_{ijk}^{abc} \{ a^\dagger i b^\dagger j c^\dagger k \} = \begin{array}{c} \downarrow \nearrow \downarrow \nearrow \downarrow \nearrow \\ \text{---} \end{array}$$

Figure 2. The Diagrammatic Representation of Coupled-Cluster Excitation Operators $T_1(X)$, $T_2(X)$ and $T_3(X)$.

$$\Delta E = \text{Diagram 1} + \text{Diagram 2} + \text{Diagram 3}$$

Figure 3. The Diagrammatic Representation of the Coupled-Cluster Energy.

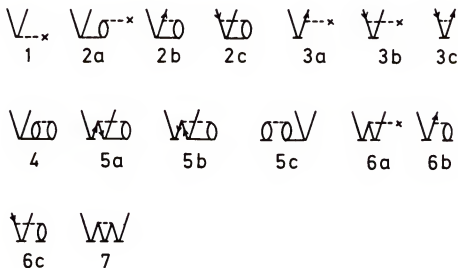


Figure 4. The Diagrammatic Representation of the $T_1(X)$ Amplitude Equation in the CCSDT Model.

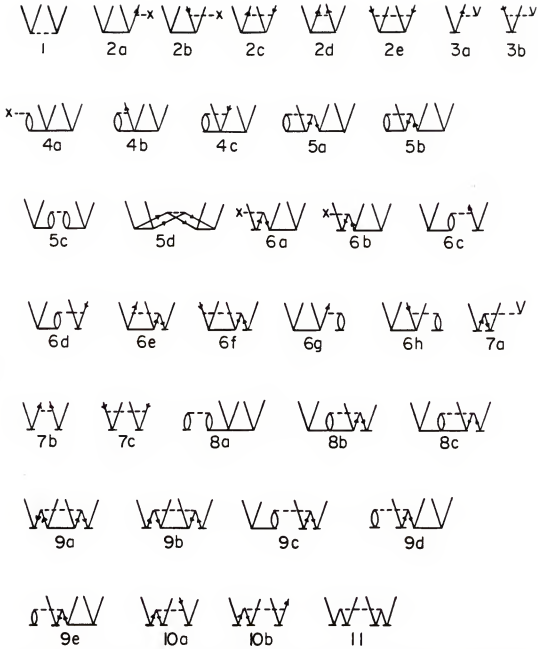


Figure 5. The Diagrammatic Representation of the $T_2(X)$ Amplitude Equation in the CCSDT Model.

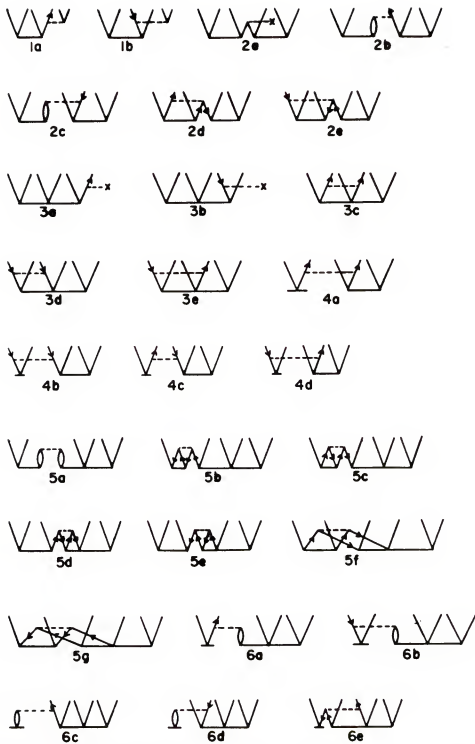


Figure 6. The Diagrammatic Representation of the $T_3(X)$ Amplitude Equation in the CCSDT Model.

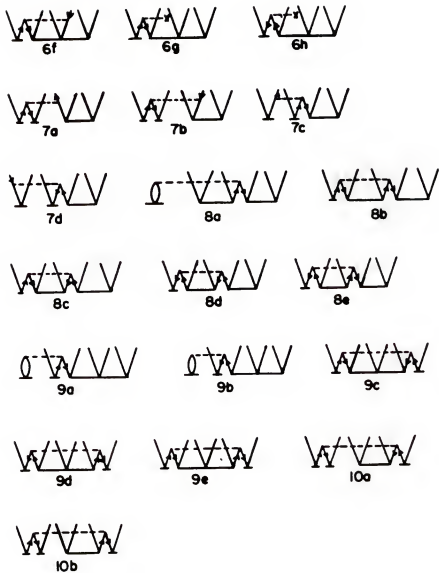


Figure 6--continued

FIRST DERIVATIVES OF THE COUPLED-CLUSTER ENERGY

Derivation of General Expressions

Let us return to Equation (6), where the Hamiltonian is in normal-ordered form and the wavefunction is the exponential of the Coupled-Cluster model.

$$e^{-T(X)} H_N(X) e^{T(X)} |0\rangle = \Delta E(X) |0\rangle \quad (10)$$

Let us define the following:

$$\begin{aligned} T &= T(X) \Big|_{X=0} & T^X &= \frac{\partial T(X)}{\partial X} \Big|_{X=0} \\ H_N &= f_N + W_N = (f_N(X) + W_N(X)) \Big|_{X=0} & H_N^X &= f_N^X + W_N^X = \left(\frac{\partial f_N(X)}{\partial X} + \frac{\partial W_N(X)}{\partial X} \right) \Big|_{X=0} \\ \Delta E &= \Delta E(X) \Big|_{X=0} & \Delta E^X &= \frac{\partial \Delta E(X)}{\partial X} \Big|_{X=0} \end{aligned}$$

Let the symbol $|P\rangle$ represent the space of orthonormal determinants in which the amplitudes of $T(X)$ and $\Delta E(X)$ are determined. Let the symbol $|\Phi\rangle$ represent the excited determinants only.

$$\hat{1} = |P\rangle\langle P| \quad (11)$$

$$|P\rangle = |0\rangle + |\Phi\rangle$$

Projection on the left by $\langle P|$ and evaluation at $\chi=0$ and yields the unperturbed Coupled-Cluster expressions.

$$\langle 0| (H_N e^T)_c |0\rangle = \Delta E \quad (12)$$

and

$$\langle \Phi| (H_N e^T)_c |0\rangle = 0 \quad (13)$$

Of course, the unperturbed CC model ($\chi=0$) is a special case of the perturbation-dependent CC model discussed in the previous section. Equations (12) and (13) are Equations (8) and (9) evaluated at $\chi=0$, respectively.

The derivative of Equation (10) with respect to χ , evaluated at $\chi=0$, is given by the following, where we have used the fact that excitation operators commute with one another:

$$\left[[(H_N e^T)_c, T^X] + (H_N^X e^T)_c \right] |0\rangle = \Delta E^X |0\rangle . \quad (14)$$

Or more simply,

$$\left[((H_N e^T)_c T^X)_c + (H_N^X e^T)_c \right] |0\rangle = \Delta E^X |0\rangle .$$

Projection on the left by $\langle P|$ yields an expression for ΔE^X and a set of linear equations which determine the derivative t-amplitudes:

$$\langle 0| ((H_N e^T)_c T^X)_c |0\rangle + \langle 0| (H_N^X e^T)_c |0\rangle = \Delta E^X \quad (15)$$

and

$$\langle \Phi| ((H_N e^T)_c T^X)_c |0\rangle + \langle \Phi| (H_N^X e^T)_c |0\rangle = 0 . \quad (16)$$

For the CCSDT model, the Equation (16) represents three coupled, linear equations for the T_1^X , T_2^X and T_3^X amplitudes. If the unperturbed CCSDT amplitudes are available, the derivative amplitude equations can be constructed and solved. The derivative energy ΔE^X can then be evaluated by Equation (15).

However, it is not necessary to solve Equation (16) for the derivative t-amplitudes in order to evaluate ΔE^X . Returning to Equation (14), we insert $\hat{1} = |P\rangle\langle P|$ into the terms involving T^X and left project by $\langle P|$ to obtain

$$\langle 0| -T^X|P\rangle\langle P|(H_N e^T)_c|0\rangle + \langle 0|(H_N^X e^T)_c|0\rangle + \langle 0|(H_N e^T)_c|P\rangle\langle P|T^X|0\rangle = \Delta E^X$$

and

$$\langle \Phi| -T^X|P\rangle\langle P|(H_N e^T)_c|0\rangle + \langle \Phi|(H_N^X e^T)_c|0\rangle + \langle \Phi|(H_N e^T)_c|P\rangle\langle P|T^X|0\rangle = 0.$$

But T^X is an excitation operator, hence $\langle 0|T^X|P\rangle=0$. Furthermore, T is the solution to the unperturbed equation $\langle \Phi|(H_N e^T)_c|0\rangle=0$. Also, recall that $\langle 0|(H_N e^T)_c|0\rangle=\Delta E$. Now we have

$$\langle 0|(H_N^X e^T)_c|0\rangle + \langle 0|(H_N e^T)_c|\Phi\rangle\langle \Phi|T^X|0\rangle = \Delta E^X$$

and

$$\langle \Phi| -T^X|0\rangle\Delta E + \langle \Phi|(H_N^X e^T)_c|0\rangle + \langle \Phi|(H_N e^T)_c|\Phi\rangle\langle \Phi|T^X|0\rangle = 0.$$

The second equation is solved for $\langle \Phi|T^X|0\rangle$:

$$\langle \Phi|T^X|0\rangle = -\langle \Phi|(H_N e^T)_c|0\rangle^{-1} \Delta E \langle \Phi|(H_N^X e^T)_c|0\rangle,$$

and we then substitute for $\langle \Phi | T^X | 0 \rangle$ in the ΔE^X expression.

$$\langle 0 | (H_N^X e^T)_c | 0 \rangle - \langle 0 | (H_N e^T)_c | \Phi \rangle \langle \Phi | (H_N e^T)_c - \Delta E | \Phi \rangle^{-1} \langle \Phi | (H_N^X e^T)_c | 0 \rangle = \Delta E^X$$

Now we define an antisymmetrized, perturbation-independent, de-excitation operator Λ . Let $\Lambda = \Lambda_1 + \Lambda_2 + \Lambda_3 + \dots$, where

$$\begin{aligned} \Lambda_1 &= \sum_{i,a} \lambda_a^i \{i^+ a\} \\ \Lambda_2 &= \frac{1}{4} \sum_{i,j} \sum_{a,b} \lambda_{ab}^{ij} \{i^+ a j^+ b\} \\ &\vdots \\ \Lambda_n &= \frac{1}{(n!)^2} \sum_{i,j,\dots} \sum_{a,b,\dots} \lambda_{ab\dots}^{ij\dots} \{i^+ a j^+ b \dots\} \\ &\vdots \end{aligned}$$

For every T_n in T we will have a corresponding Λ_n in Λ . That is, for the CCD model we have the truncation $\Lambda = \Lambda_2$. For the CCSD model we have $\Lambda = \Lambda_1 + \Lambda_2$, and for the CCSDT model we have $\Lambda = \Lambda_1 + \Lambda_2 + \Lambda_3$. We require that the λ -amplitudes satisfy the condition:

$$\langle 0 | \Lambda | \Phi \rangle = - \langle 0 | (H_N e^T)_c | \Phi \rangle \langle \Phi | (H_N e^T)_c - \Delta E | \Phi \rangle^{-1}.$$

By defining Λ in this manner, we obtain an expression for ΔE^X that is not dependent upon T^X . We have

$$\langle 0 | (H_N^X e^T)_c | 0 \rangle + \langle 0 | \Lambda | \Phi \rangle \langle \Phi | (H_N^X e^T)_c | 0 \rangle = \Delta E^X ,$$

which can be evaluated if we first solve

$$\langle 0 | \Lambda | \Phi \rangle \langle \Phi | (H_N e^T)_c - \Delta E | \Phi \rangle + \langle 0 | (H_N e^T)_c | \Phi \rangle = 0 .$$

Analogous steps have been often used in recent derivative literature to reduce the number of linear equations to be solved from $3N$ to just one. The method is sometimes referred to as the Z-vector method of Handy.^{22,34}

We now wish to find equivalent forms of the above expressions which can be readily subjected to the usual diagrammatic rules. Recalling that $\hat{1} = |P\rangle\langle P| = |0\rangle\langle 0| + |\Phi\rangle\langle\Phi|$, the derivative energy can be written as:

$$\Delta E^X = \langle 0 | (H_N^X e^T)_c | 0 \rangle + \langle 0 | \Lambda (H_N^X e^T)_c | 0 \rangle , \quad (17)$$

and the Λ equations can be written as

$$\langle 0 | \Lambda (H_N e^T)_c | \Phi \rangle - \Delta E \langle 0 | \Lambda | \Phi \rangle + \langle 0 | (H_N e^T)_c | \Phi \rangle = 0 .$$

If we consider

$$\begin{aligned} \langle 0 | (H_N e^T)_c \Lambda | \Phi \rangle &= \langle 0 | (H_N e^T)_c | P \rangle \langle P | \Lambda | \Phi \rangle \\ &= \langle 0 | (H_N e^T)_c | 0 \rangle \langle 0 | \Lambda | \Phi \rangle + \langle 0 | (H_N e^T)_c | \Phi \rangle \langle \Phi | \Lambda | \Phi \rangle \\ &= \Delta E \langle 0 | \Lambda | \Phi \rangle + \langle 0 | (H_N e^T)_c | \Phi \rangle \langle \Phi | \Lambda | \Phi \rangle , \end{aligned}$$

then it is clear that we may write the Λ equations in terms of the commutator $[\Lambda, (H_N e^T)_c]$. Of the commutator, of course, only the connected product is non-zero. Finally, the Λ equations become:

$$\langle 0 | (\Lambda (H_N e^T)_c) | \Phi \rangle + \langle 0 | (H_N e^T)_c | \Phi \rangle \langle \Phi | \Lambda | \Phi \rangle + \langle 0 | (H_N e^T)_c | \Phi \rangle = 0 \quad (18)$$

Equations (17) and (18) summarize the CC energy derivative. In Equation (17), ΔE^X is expressed in terms of unperturbed t -amplitudes, the derivative integrals of H_N and the λ -amplitudes. Equation (18) is the coupled, linear set of equations which determine the λ -amplitudes. The equations are general in that they apply to CC models of any choice of truncation of T (and the corresponding choice of Λ and projection space $|P\rangle$). Also, the equations apply to CC models where non-Hartree-Fock orbitals are chosen as the spin-orbital basis, as well as when SCF orbitals are chosen. The equations apply generally to CC models for open-shell systems, where Unrestricted Hartree-Fock (UHF) orbitals are used, or other different-orbitals-for-different-spin cases.

The diagrammatic representation of the H_N^X operator and the Λ operators are given in Figures (7) and (8), respectively. The fully-contracted products which contribute to the CCSDT derivative energy expression are represented diagrammatically in Figure (9). The algebraic expression for the CCSDT derivative energy is given in Table (1); each term corresponds to a diagram in Figure (9) and is so labeled.

In the CCSDT model, Equation (18) represents three coupled, linear equations which determine the amplitudes of the Λ_1 , Λ_2 , and Λ_3

operators:

$$\langle 0 | (\Lambda (H_N e^T)_c) | S \rangle + \langle 0 | (H_N e^T)_c | S \rangle = 0$$

$$\langle 0 | (\Lambda (H_N e^T)_c) | D \rangle + \langle 0 | (H_N e^T)_c | S \rangle \langle S | \Lambda | D \rangle + \langle 0 | (H_N e^T)_c | D \rangle = 0$$

$$\langle 0 | (\Lambda (H_N e^T)_c) | T \rangle + \langle 0 | (H_N e^T)_c | S \rangle \langle S | \Lambda | T \rangle + \langle 0 | (H_N e^T)_c | D \rangle \langle D | \Lambda | T \rangle = 0.$$

The above equations are represented diagrammatically in Figures (10-12). The algebraic interpretations of the diagrammatic equations are given in Tables (2-4), respectively. Note that although there are disconnected parts of the Λ_2 and Λ_3 amplitude equations, there are no closed and disconnected parts; the energy derivative is necessarily linked. For the CCSD model and restricted Hartree-Fock (RHF) orbitals, the Λ_1 and Λ_2 equations are of course equivalent to that obtained by Scheiner et al.²⁷

In Tables (3) and (4) we use the symbol $P(\text{occ})$ (or $P(\text{vir})$) to represent an operator that generates a sum over the permutations of occupied (or virtual) labels contained in parentheses, with each permutation carrying a parity factor. Specifically, the symbol $P(pq)$ found in Table (3) has the meaning:

$$P(pq) = \text{identity} - \text{interchange } p \leftrightarrow q.$$

The symbol $P(p/qr)$ found in Table (4) has the meaning:

$$P(p/qr) = \text{identity} - \text{interchange } p \leftrightarrow q - \text{interchange } p \leftrightarrow r,$$

where the slash indicates that the labels q and r are actually equivalent--permutations which interchange q and r are not generated. The symbol $P(\text{vir}|\text{occ})$ is the product of the permutations of $P(\text{vir})$ and $P(\text{occ})$. For example, the symbol $P(\text{ab}|\text{ij})$, found in Table (3), generates four terms:

$$\begin{aligned} P(\text{ab}|\text{ij}) = & \text{identity} - \text{interchange } a \bullet b - \text{interchange } i \bullet j \\ & + \text{interchange } a \bullet b \text{ and } i \bullet j \quad . \end{aligned}$$

Finally, the symbol $P(\text{a/bc}|\text{i/jk})$, found in Table (4) generates nine terms:

$$\begin{aligned} P(\text{a/bc}|\text{i/jk}) = & \text{identity} - \text{interchange } a \bullet b - \text{interchange } a \bullet c \\ & - \text{interchange } i \bullet j - \text{interchange } i \bullet k \\ & + \text{interchange } a \bullet b \text{ and } i \bullet j + \text{interchange } a \bullet b \text{ and } i \bullet k \\ & + \text{interchange } a \bullet c \text{ and } i \bullet j + \text{interchange } a \bullet c \text{ and } i \bullet k \quad . \end{aligned}$$

Comparison of the λ -amplitude equations with the unperturbed t -amplitude equations (i.e., Figures (4-6), evaluated at $\chi=0$) reveals that the λ -amplitude equations possess several diagrams which are "upside-down" versions of diagrams in the t -amplitude equations. The algebraic interpretations of such diagrams are related by complex-conjugation; if the spin-orbital basis functions are real, the expressions are equivalent. For the linearized CC models, there is a one-to-one correspondence between the diagrams in the λ - and t -amplitude equations; hence, the λ -amplitudes are equivalent to the unperturbed t -amplitudes. Consider the LCCD model, where $T=T_2$ and the quadratic T_2 contributions to T_2 are not permitted. Specifically, the

T_2 equation to be solved consists only of diagrams (1) and (2a-e) in Figure (5). The corresponding Λ_2 equation will be restricted to diagrams (1) and (8-12) in Figure (11); each diagram matches a diagram in the T_2 equation. The Λ equations are, as already mentioned, linear equations; thus, for the CCD model, the Λ_2 equation must differ from the T_2 equation in that the quadratic diagrams (5a-d) in Figure (5) are absent. Instead, we find the similar, related diagrams (21-27) in Figure (11). If we denote the quadratic contributions to T_2 by the function $Q_{ij}^{ab}(I, t, x)$ the related contributions to Λ_2 are given by $Q_{ij}^{ab}(t, I, x) + Q_{ij}^{ab}(t, x, I)$.

For models including T_1 , we have previously identified the linear contributions of T_1 to T_2 , represented by diagrams (3a,b) in Figure (5); analogously there are linear contributions of Λ_1 to Λ_2 --diagrams (4,5) in Figure (11). For models including T_3 , we have previously identified the linear contributions of T_3 to T_2 , represented by diagrams (4a-c) in Figure (5); analogously there are linear contributions of Λ_3 to Λ_2 --diagrams (33-35). Consider the constant part of T_1 and linear contributions of T_1 , T_2 and T_3 to T_1 , represented by diagrams (1), (3a-c), (2a-c) and (4) in Figure (4). Analogous diagrams are present in the Λ_1 equation where Λ_1 , Λ_2 and Λ_3 take the roles of T_1 , T_2 and T_3 , respectively. The analogous diagrams are diagrams (1), (3-5), (25-27), and (78) in Figure (10). Finally, consider the linear contributions of T_2 and T_3 to T_3 , represented by diagrams (1a,b) and (3a-e) in Figure (6). (Note: there are no linear contributions of T_1 to T_3 .) Analogous diagrams are present in the Λ_3 equation: diagrams (4,5) and (8-11) in Figure (12).

The equivalence of Λ and T in the linearized CC models can be used to advantage in the evaluation of the finite-order MBPT derivatives,

since the low-order iterates of Λ and T are linear and therefore equivalent. Only the fourth-order contributions from quadruples $Q(4)$ will require special consideration. It is apparent that once the equations for Λ_1 and Λ_2 for the CCSD model have been programmed, the Λ_1 and Λ_2 equations for the CCSDT-1 model will follow readily. The same routines developed for inclusion of linear triples in the CCSDT-1 t-amplitude equations can be employed for the λ -equations. The CCSDT-1 triples routines naturally take advantage of the fact that since T_3 amplitudes are linearly dependent upon the T_2 amplitudes, it is not necessary to store the T_3 amplitudes at any time during the CC iterations. Rather, the back-contributions of T_3 to T_2 and to T_1 are computed as needed.

In order to evaluate the CCSDT energy expression given in Table (1), the remaining perturbation-dependent parts of ΔE^X --the contributions arising from the derivative integrals in the f_N^X and w_N^X operators--must be made explicit. Recall that the integrals involve the one-electron spin-orbital basis functions $\{\phi(X)\}$. Since the orbital basis functions are usually linear combinations of some primitive set of atomic orbital (AO) basis functions $\{\psi(X)\}$, the orbital basis functions are in general dependent upon X in two ways: the primitive AO functions may be dependent upon X ; the coefficients may be dependent upon X . Derivative integral programs provide the derivatives of one and two-electron integrals over the primitive basis functions. Coupled-Perturbed Hartree-Fock (CPHF) theory^{15,35} provides the derivatives of the SCF orbital coefficients. In the following sections, we exclusively consider the choice of SCF orbitals as the spin-orbital basis.

$$f_{pq}^x \{p^\dagger q\} =$$

$$\langle pq || rs \rangle^x \{p^\dagger q^\dagger sr\} =$$

Figure 7. The Diagrammatic Representation of H_N^X .

$$\lambda_a^i \{i^\dagger a\} =$$



$$\lambda_{ab}^{ij} \{i^\dagger a j^\dagger b\} =$$



$$\lambda_{abc}^{ijk} \{i^\dagger a j^\dagger b k^\dagger c\} =$$



Figure 8. The Diagrammatic Representation of the De-excitation Operators λ_1 , λ_2 , and λ_3 .

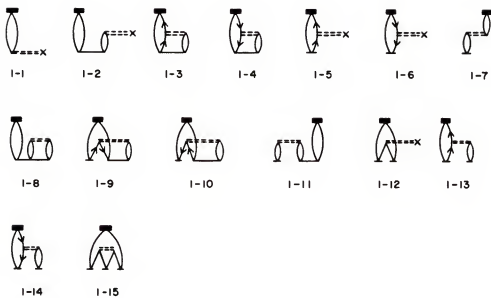
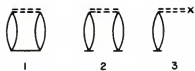


Figure 9. The Diagrammatic Representation of the Coupled-Cluster Energy Derivative.

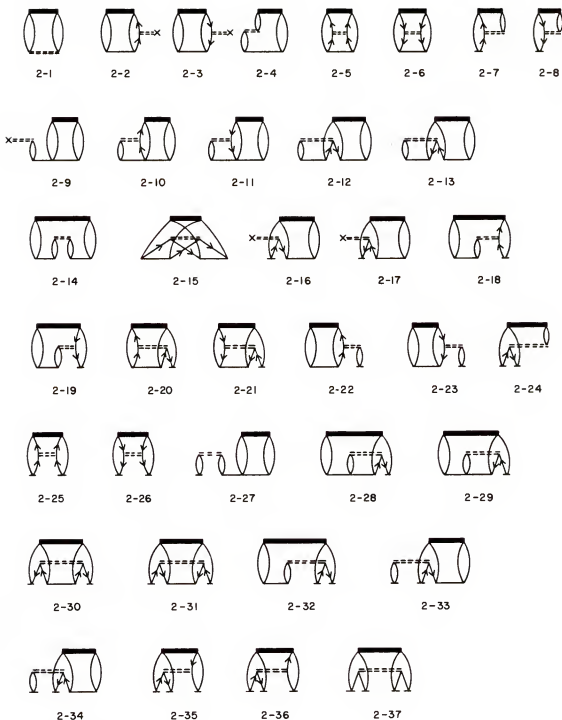


Figure 9--continued

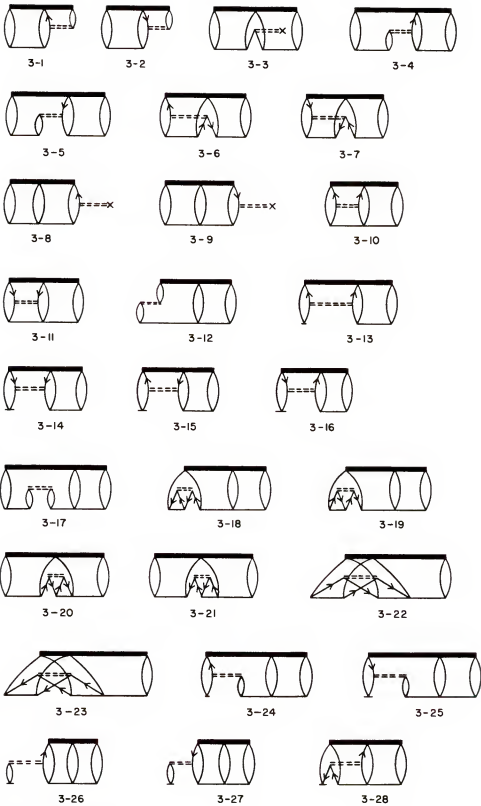


Figure 9--continued

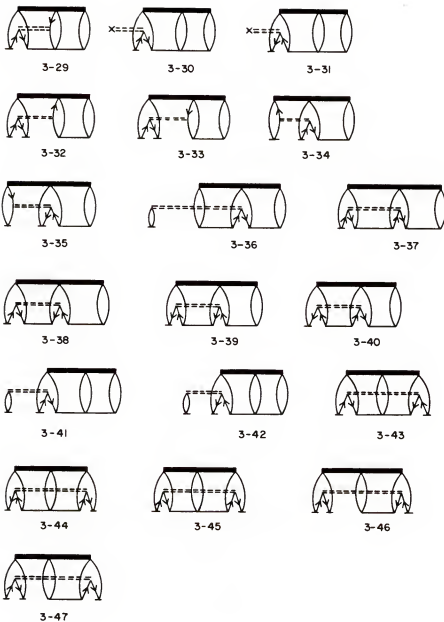


Figure 9--continued

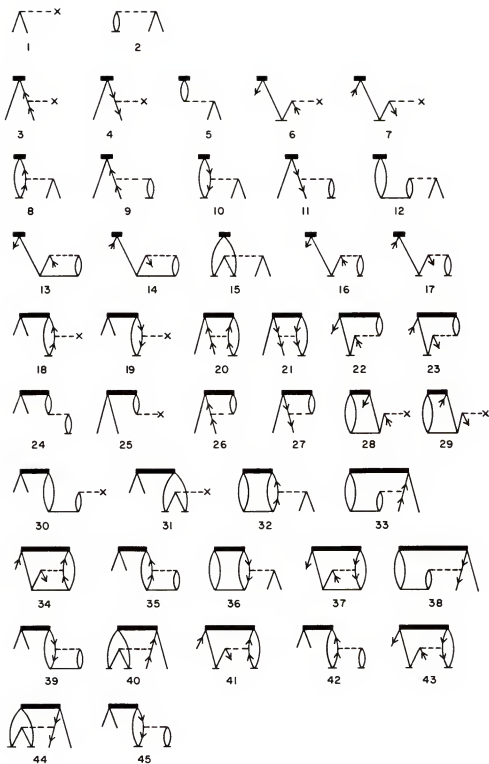


Figure 10. The Diagrammatic Representation of the Λ_1 Equation in the CCSDT Derivative Model.

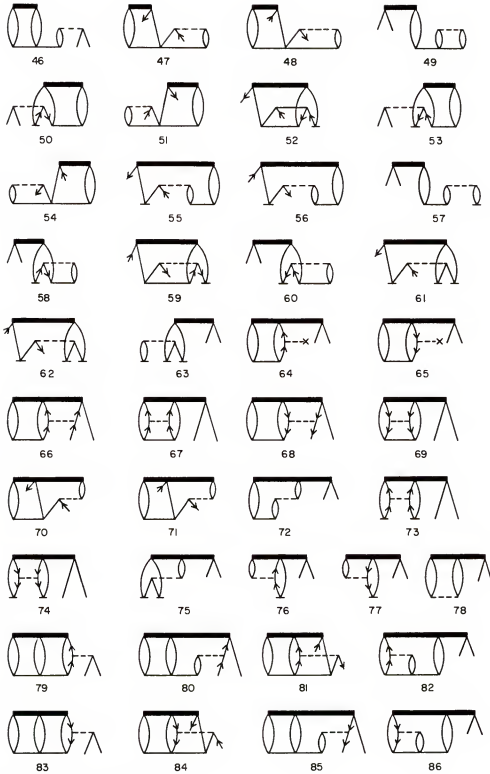


Figure 10--continued

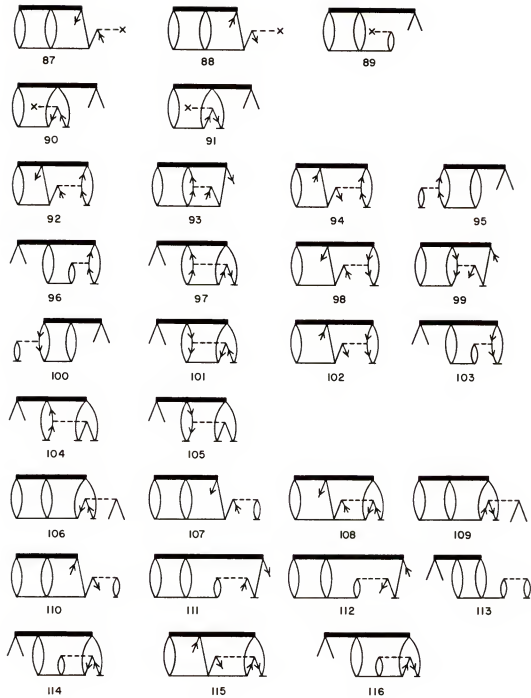


Figure 10--continued

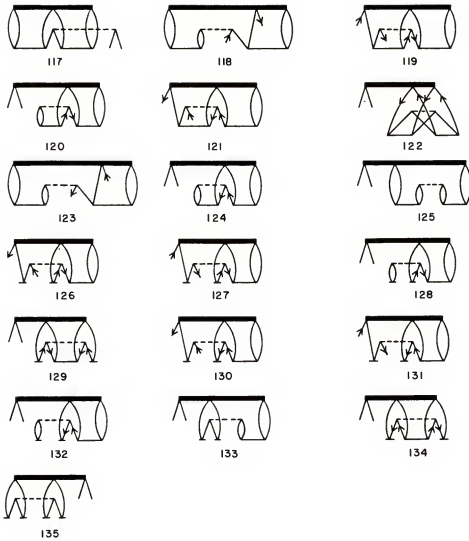


Figure 10--continued

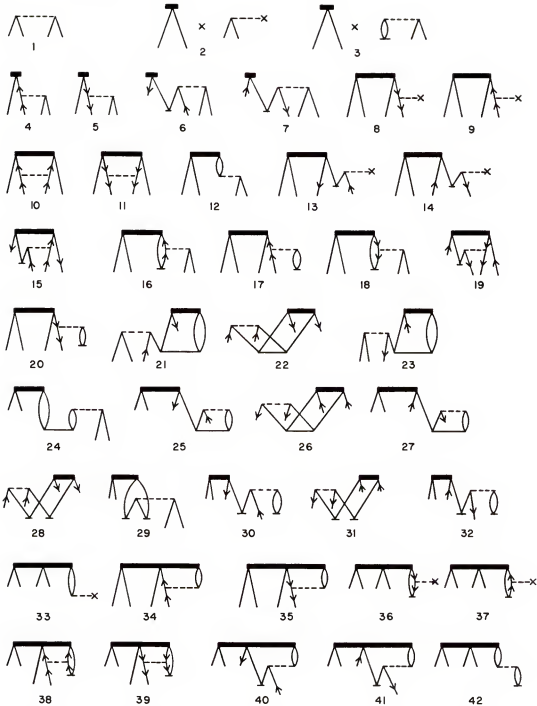


Figure 11. The Diagrammatic Representation of the Λ_2 Equation in the CCSDT Derivative Model.

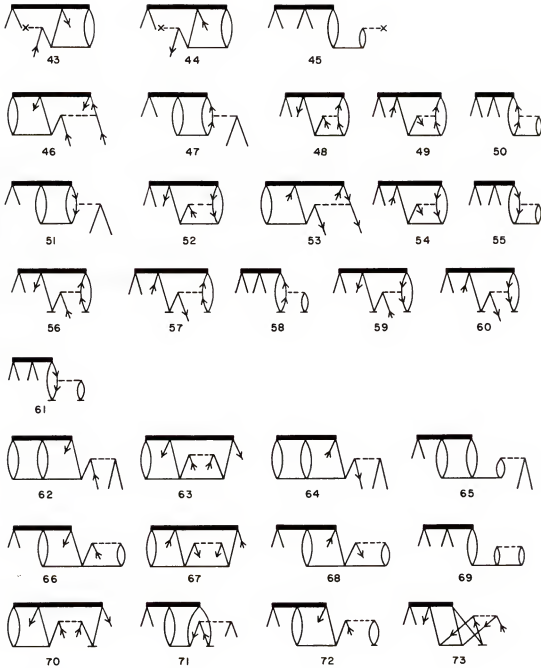


Figure 11--continued

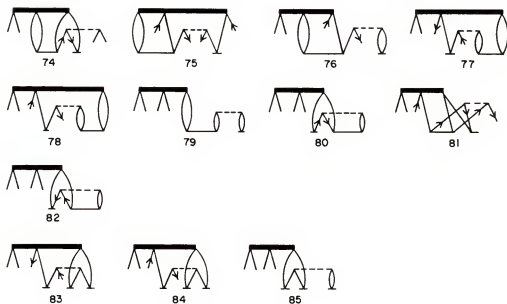


Figure 11--continued

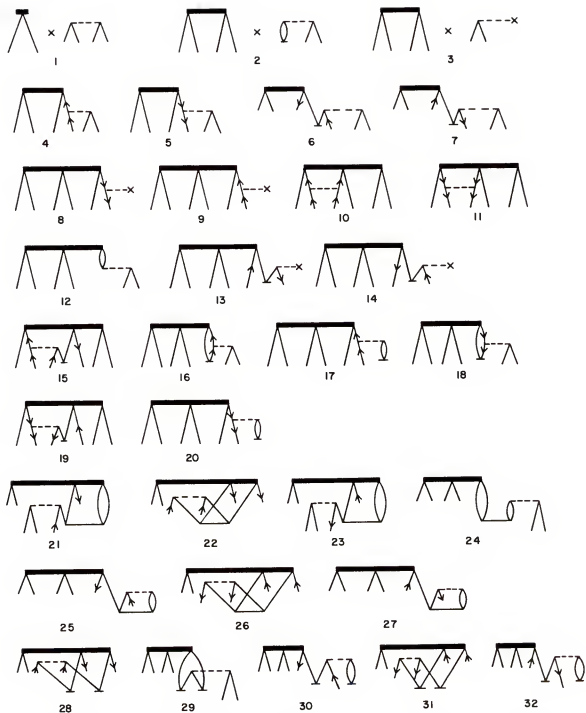


Figure 12. The Diagrammatic Representation of the Λ_3 Equation in the CCSDT Derivative Model.

Table 1. The CCSDT Derivative Energy Expression.

$$\begin{aligned}
\Delta E^X &= \frac{1}{4} t_{ij}^{ab} \langle ij || ab \rangle^X & [1] \\
&+ \frac{1}{2} t_i^a t_j^b \langle ij || ab \rangle^X & [2] \\
&+ t_i^a f_{ia}^X & [3] \\
&+ \lambda_a^i f_{ai}^X & [1-1] \\
&- \lambda_a^i f_{ji}^X t_j^a & [1-6] \\
&+ \lambda_a^i f_{ab}^X t_i^b & [1-5] \\
&+ \lambda_a^i \langle ja || bi \rangle^X t_j^b & [1-7] \\
&+ \lambda_b^j f_{ia}^X t_{ji}^{ba} & [1-2] \\
&+ \frac{1}{2} \lambda_a^j \langle ai || bc \rangle^X t_{ji}^{bc} & [1-3] \\
&- \frac{1}{2} \lambda_b^i \langle jk || ia \rangle^X t_{jk}^{ba} & [1-4] \\
&- \lambda_b^j f_{ia}^X t_i^b t_j^a & [1-12] \\
&+ \lambda_a^j \langle ai || bc \rangle^X t_j^b t_i^c & [1-13] \\
&- \lambda_b^i \langle jk || ia \rangle^X t_j^b t_k^a & [1-14] \\
&+ \frac{1}{4} \lambda_c^k \langle ij || ab \rangle^X t_{kij}^{cab} & [1-8] \\
&+ \lambda_c^k \langle ij || ab \rangle^X t_{ki}^{ca} t_j^b & [1-11] \\
&+ \frac{1}{2} \lambda_c^k \langle ij || ab \rangle^X t_{ij}^{ca} t_k^b & [1-9] \\
&+ \frac{1}{2} \lambda_c^k \langle ij || ab \rangle^X t_{ki}^{ab} t_j^c & [1-10] \\
&+ \lambda_c^k \langle ij || ab \rangle^X t_k^a t_i^b t_j^c & [1-15] \\
&+ \frac{1}{4} \lambda_{ab}^{ij} \langle ab || ij \rangle^X & [2-1] \\
&- \frac{1}{2} \lambda_{ab}^{ij} \langle ab || ci \rangle^X t_j^c & [2-7] \\
&+ \frac{1}{2} \lambda_{ab}^{ij} \langle ka || ij \rangle^X t_k^b & [2-8]
\end{aligned}$$

Table 1--continued

$+ \frac{1}{2} \lambda_{ab}^{ik} f_{ji} X t_{kj}^{ab}$	[2-3]
$- \frac{1}{2} \lambda_{ac}^{ij} f_{ab} X t_{ij}^{cb}$	[2-2]
$+ \frac{1}{8} \lambda_{ab}^{ij} \langle ab cd \rangle X t_{ij}^{cd}$	[2-5]
$+ \frac{1}{8} \lambda_{ab}^{ij} \langle kl ij \rangle X t_{kl}^{ab}$	[2-6]
$+ \lambda_{ac}^{ik} \langle ja bi \rangle X t_{kj}^{cb}$	[2-4]
$+ \frac{1}{4} \lambda_{ab}^{ji} \langle ab cd \rangle X t_j^c t_i^d$	[2-25]
$+ \frac{1}{4} \lambda_{ba}^{ij} \langle kl ij \rangle X t_k^b t_l^a$	[2-26]
$- \lambda_{ac}^{ik} \langle ja bi \rangle X t_j^c t_k^b$	[2-24]
$+ \frac{1}{4} \lambda_{cb}^{kj} f_{ia} X t_{kji}^{cba}$	[2-9]
$- \frac{1}{4} \lambda_{ad}^{kj} \langle ai bc \rangle X t_{kji}^{dbc}$	[2-10]
$+ \frac{1}{4} \lambda_{cb}^{il} \langle jk ia \rangle X t_{ljk}^{cba}$	[2-11]
$- \frac{1}{2} \lambda_{bc}^{jk} f_{ia} X t_{ji}^{bc} t_k^a$	[2-16]
$- \frac{1}{2} \lambda_{bc}^{jk} f_{ia} X t_{jk}^{ba} t_i^c$	[2-17]
$- \frac{1}{2} \lambda_{ad}^{jk} \langle ai bc \rangle X t_{jk}^{db} t_i^c$	[2-22]
$+ \lambda_{ad}^{jk} \langle ai bc \rangle X t_{ji}^{db} t_k^c$	[2-18]
$- \frac{1}{4} \lambda_{ad}^{jk} \langle ai bc \rangle X t_{jk}^{bc} t_i^d$	[2-20]
$+ \frac{1}{2} \lambda_{bc}^{il} \langle jk ia \rangle X t_{lj}^{bc} t_k^a$	[2-23]
$+ \frac{1}{4} \lambda_{bc}^{il} \langle jk ia \rangle X t_{jk}^{bc} t_l^a$	[2-21]
$- \lambda_{bc}^{il} \langle jk ia \rangle X t_{lj}^{ba} t_k^c$	[2-19]
$- \frac{1}{2} \lambda_{ad}^{kj} \langle ai bc \rangle X t_k^b t_i^d t_j^c$	[2-36]
$+ \frac{1}{2} \lambda_{cb}^{il} \langle jk ia \rangle X t_j^c t_k^b t_l^a$	[2-35]

Table 1--continued

$+ \frac{1}{4} \lambda_{dc}^{lk} \langle ij ab \rangle^X t_{lki}^{dca} t_j^b$	[2-27]
$+ \frac{1}{4} \lambda_{dc}^{lk} \langle ij ab \rangle^X t_{lij}^{dca} t_k^b$	[2-29]
$+ \frac{1}{4} \lambda_{dc}^{lk} \langle ij ab \rangle^X t_{lki}^{dab} t_j^c$	[2-28]
$+ \frac{1}{2} \lambda_{cd}^{kl} \langle ij ab \rangle^X t_{ki}^{ca} t_{lj}^{db}$	[2-14]
$- \frac{1}{4} \lambda_{cd}^{kl} \langle ij ab \rangle^X t_{ij}^{ca} t_{kl}^{db}$	[2-13]
$+ \frac{1}{16} \lambda_{cd}^{kl} \langle ij ab \rangle^X t_{kl}^{ab} t_{ij}^{cd}$	[2-15]
$- \frac{1}{4} \lambda_{cd}^{kl} \langle ij ab \rangle^X t_{ki}^{ab} t_{lj}^{cd}$	[2-12]
$- \frac{1}{2} \lambda_{cd}^{kl} \langle ij ab \rangle^X t_{ki}^{cd} t_l^a t_j^b$	[2-33]
$+ \frac{1}{8} \lambda_{cd}^{lk} \langle ij ab \rangle^X t_{ij}^{cd} t_l^a t_k^b$	[2-31]
$- \frac{1}{2} \lambda_{cd}^{kl} \langle ij ab \rangle^X t_{kl}^{ca} t_i^d t_j^b$	[2-34]
$- \lambda_{cd}^{kl} \langle ij ab \rangle^X t_{ki}^{ca} t_j^d t_l^b$	[2-32]
$+ \frac{1}{8} \lambda_{dc}^{kl} \langle ij ab \rangle^X t_{kl}^{ab} t_i^d t_j^c$	[2-30]
$+ \frac{1}{4} \lambda_{dc}^{kl} \langle ij ab \rangle^X t_i^d t_j^c t_k^a t_l^b$	[2-37]
$+ \frac{1}{4} \lambda_{abd}^{ikj} \langle ab ci \rangle^X t_{kj}^{dc}$	[3-1]
$- \frac{1}{4} \lambda_{acb}^{ijl} \langle ka ij \rangle^X t_{lk}^{cb}$	[3-2]
$- \frac{1}{12} \lambda_{abc}^{ilk} f_{ji}^X t_{lkj}^{abc}$	[3-9]
$+ \frac{1}{12} \lambda_{adc}^{ijk} f_{ab}^X t_{ijk}^{dcb}$	[3-8]
$+ \frac{1}{24} \lambda_{abe}^{ijk} \langle ab cd \rangle^X t_{ijk}^{ecd}$	[3-10]
$+ \frac{1}{24} \lambda_{abc}^{ijm} \langle kl ij \rangle^X t_{mkl}^{abc}$	[3-11]
$+ \frac{1}{4} \lambda_{adc}^{ilk} \langle ja bi \rangle^X t_{lkj}^{dcb}$	[3-12]
$+ \frac{1}{4} \lambda_{abe}^{jki} \langle ab cd \rangle^X t_{jk}^{ec} t_i^d$	[3-13]

Table 1--continued

$+ \frac{1}{4} \lambda_{bca}^{ijm} \langle kl ij \rangle^X t_{mk}^{bc} t_l^a$	[3-14]
$- \frac{1}{2} \lambda_{adc}^{ikl} \langle ja bi \rangle^X t_{kj}^{dc} t_l^b$	[3-15]
$- \frac{1}{2} \lambda_{acd}^{ilk} \langle ja bi \rangle^X t_{lk}^{cb} t_j^d$	[3-16]
$- \frac{1}{12} \lambda_{bcd}^{jkl} f_{ia}^X t_{jki}^{bcd} t_l^a$	[3-30]
$- \frac{1}{12} \lambda_{bcd}^{jkl} f_{ia}^X t_{jkl}^{bca} t_i^d$	[3-31]
$+ \frac{1}{12} \lambda_{ade}^{jkl} \langle ai bc \rangle^X t_{jkl}^{deb} t_i^c$	[3-26]
$- \frac{1}{4} \lambda_{ade}^{jkl} \langle ai bc \rangle^X t_{jki}^{deb} t_l^c$	[3-24]
$+ \frac{1}{12} \lambda_{ade}^{jkl} \langle ai bc \rangle^X t_{jkl}^{dbc} t_i^e$	[3-28]
$- \frac{1}{12} \lambda_{bcd}^{ilm} \langle jk ia \rangle^X t_{lmj}^{bcd} t_k^a$	[3-27]
$- \frac{1}{12} \lambda_{bcd}^{ilm} \langle jk ia \rangle^X t_{ljk}^{bcd} t_m^a$	[3-29]
$+ \frac{1}{4} \lambda_{bcd}^{ilm} \langle jk ia \rangle^X t_{lmj}^{bca} t_k^d$	[3-25]
$+ \frac{1}{4} \lambda_{cdb}^{klj} f_{ia}^X t_{kl}^{ca} t_{ji}^{db}$	[3-3]
$+ \frac{1}{8} \lambda_{aed}^{klj} \langle ai bc \rangle^X t_{ki}^{ed} t_{lj}^{bc}$	[3-6]
$- \frac{1}{2} \lambda_{aed}^{klj} \langle ai bc \rangle^X t_{kl}^{db} t_{ji}^{ec}$	[3-4]
$- \frac{1}{8} \lambda_{cdb}^{iml} \langle jk ia \rangle^X t_{jk}^{cd} t_{ml}^{ba}$	[3-7]
$+ \frac{1}{2} \lambda_{cdb}^{ilm} \langle jk ia \rangle^X t_{lj}^{ca} t_{mk}^{db}$	[3-5]
$+ \frac{1}{4} \lambda_{aed}^{kjl} \langle ai bc \rangle^X t_{ki}^{ed} t_j^b t_l^c$	[3-34]
$+ \frac{1}{2} \lambda_{aed}^{klj} \langle ai bc \rangle^X t_{kl}^{eb} t_i^d t_j^c$	[3-32]
$- \frac{1}{2} \lambda_{cdb}^{ilm} \langle jk ia \rangle^X t_{lj}^{cd} t_k^b t_m^a$	[3-33]
$- \frac{1}{4} \lambda_{cbd}^{iml} \langle jk ia \rangle^X t_{ml}^{ca} t_j^b t_k^d$	[3-35]
$- \frac{1}{24} \lambda_{cde}^{klm} \langle ij ab \rangle^X t_{kli}^{cde} t_{mj}^{ab}$	[3-19]

Table 1--continued

$+ \frac{1}{48} \lambda_{cde}^{klm} \langle ij ab \rangle^X t_{kij}^{cde} t_{lm}^{ab}$	[3-22]
$- \frac{1}{24} \lambda_{cde}^{klm} \langle ij ab \rangle^X t_{klm}^{cda} t_{ij}^{eb}$	[3-18]
$+ \frac{1}{4} \lambda_{cde}^{klm} \langle ij ab \rangle^X t_{kli}^{cda} t_{mj}^{eb}$	[3-17]
$- \frac{1}{8} \lambda_{cde}^{klm} \langle ij ab \rangle^X t_{kij}^{cda} t_{lm}^{eb}$	[3-20]
$+ \frac{1}{48} \lambda_{cde}^{klm} \langle ij ab \rangle^X t_{klm}^{cab} t_{ij}^{de}$	[3-23]
$- \frac{1}{8} \lambda_{cde}^{klm} \langle ij ab \rangle^X t_{kli}^{cab} t_{mj}^{de}$	[3-21]
$- \frac{1}{12} \lambda_{cde}^{klm} \langle ij ab \rangle^X t_{kli}^{cde} t_m^a t_j^b$	[3-41]
$+ \frac{1}{24} \lambda_{cde}^{kml} \langle ij ab \rangle^X t_{kij}^{cde} t_m^a t_l^b$	[3-43]
$- \frac{1}{12} \lambda_{cde}^{klm} \langle ij ab \rangle^X t_{klm}^{cda} t_i^e t_j^b$	[3-42]
$- \frac{1}{4} \lambda_{cde}^{klm} \langle ij ab \rangle^X t_{kli}^{cda} t_j^e t_m^b$	[3-45]
$+ \frac{1}{24} \lambda_{ced}^{klm} \langle ij ab \rangle^X t_{klm}^{cab} t_i^e t_j^d$	[3-44]
$+ \frac{1}{4} \lambda_{dec}^{lmk} \langle ij ab \rangle^X t_{li}^{de} t_{mk}^{ca} t_j^b$	[3-36]
$- \frac{1}{2} \lambda_{dec}^{lkm} \langle ij ab \rangle^X t_{li}^{de} t_{kj}^{ca} t_m^b$	[3-37]
$+ \frac{1}{8} \lambda_{dec}^{lmk} \langle ij ab \rangle^X t_{li}^{de} t_{mk}^{ab} t_j^c$	[3-40]
$+ \frac{1}{8} \lambda_{dec}^{mkl} \langle ij ab \rangle^X t_{ij}^{de} t_{mk}^{ca} t_l^b$	[3-38]
$- \frac{1}{2} \lambda_{dce}^{lmk} \langle ij ab \rangle^X t_{lm}^{da} t_{ki}^{cb} t_j^e$	[3-39]
$+ \frac{1}{4} \lambda_{dec}^{lkm} \langle ij ab \rangle^X t_{li}^{de} t_j^c t_k^a t_m^b$	[3-46]
$+ \frac{1}{4} \lambda_{dce}^{lmk} \langle ij ab \rangle^X t_{lm}^{da} t_i^c t_j^e t_k^b$	[3-47]

Note: Summation over all labels is implied.

Table 2. The Λ_1 Equation for the CCSDT Derivative Model.

$$\begin{aligned}
0 = & f_{ia} + \langle ji || ba \rangle t_j^b \\
& + \lambda_b^i f_{ba} \\
& - \lambda_a^j f_{ij} \\
& + \lambda_b^j \langle ib || aj \rangle \\
& - \lambda_b^i f_{ja} t_j^b \\
& - \lambda_a^j f_{ib} t_j^b \\
& + \lambda_c^j \langle ci || ba \rangle t_j^b \\
& - \lambda_c^i \langle cj || ba \rangle t_j^b \\
& - \lambda_b^k \langle ji || ka \rangle t_j^b \\
& + \lambda_a^k \langle ji || kb \rangle t_j^b \\
& + \lambda_b^j \langle ki || ca \rangle t_{jk}^{bc} \\
& + \frac{1}{2} \lambda_b^i \langle jk || ca \rangle t_{jk}^{bc} \\
& + \frac{1}{2} \lambda_a^j \langle ki || bc \rangle t_{jk}^{bc} \\
& - \lambda_c^j \langle ki || ba \rangle t_k^c t_j^b \\
& + \lambda_c^i \langle kj || ba \rangle t_k^c t_j^b \\
& + \lambda_a^k \langle ji || cb \rangle t_k^c t_j^b \\
& + \lambda_{ca}^{ji} f_{cb} t_j^b \\
& - \lambda_{ba}^{ki} f_{jk} t_j^b \\
& + \frac{1}{2} \lambda_{cd}^{ji} \langle cd || ba \rangle t_j^b \\
& + \frac{1}{2} \lambda_{ba}^{kl} \langle ji || kl \rangle t_j^b \\
& - \lambda_{cb}^{ki} \langle jc || ak \rangle t_j^b
\end{aligned}$$

Table 2--continued

-	λ_{ca}^{kj}	$\langle ic bk \rangle$	t_j^b
+	λ_{ca}^{ki}	$\langle jc bk \rangle$	t_j^b
+	λ_{ba}^{ji}	f_{bj}	
-	$\frac{1}{2}$	λ_{bc}^{ji}	$\langle bc aj \rangle$
+	$\frac{1}{2}$	λ_{ba}^{jk}	$\langle ib jk \rangle$
-	$\frac{1}{2}$	λ_{bc}^{ji}	$f_{ka} t_{jk}^{bc}$
-	$\frac{1}{2}$	λ_{ba}^{jk}	$f_{ic} t_{jk}^{bc}$
+	λ_{ba}^{ji}	$f_{kc} t_{jk}^{bc}$	
-	λ_{ca}^{ji}	$f_{kb} t_k^c t_j^b$	
-	$\frac{1}{2}$	λ_{db}^{jk}	$\langle di ca \rangle t_{jk}^{bc}$
+	λ_{db}^{ji}	$\langle dk ca \rangle t_{jk}^{bc}$	
-	$\frac{1}{4}$	λ_{da}^{jk}	$\langle di bc \rangle t_{jk}^{bc}$
+	$\frac{1}{2}$	λ_{da}^{ji}	$\langle dk bc \rangle t_{jk}^{bc}$
+	$\frac{1}{2}$	λ_{bc}^{lj}	$\langle ki la \rangle t_{jk}^{bc}$
+	$\frac{1}{4}$	λ_{bc}^{li}	$\langle jk la \rangle t_{jk}^{bc}$
-	λ_{ba}^{lj}	$\langle ki lc \rangle t_{jk}^{bc}$	
-	$\frac{1}{2}$	λ_{ba}^{li}	$\langle jk lc \rangle t_{jk}^{bc}$
-	λ_{dc}^{ji}	$\langle dk ba \rangle t_k^c t_j^b$	
-	$\frac{1}{2}$	λ_{da}^{kj}	$\langle di cb \rangle t_k^c t_j^b$
+	λ_{da}^{ki}	$\langle dj cb \rangle t_k^c t_j^b$	
+	$\frac{1}{2}$	λ_{cb}^{li}	$\langle kj la \rangle t_k^c t_j^b$

Table 2--continued

+	λ_{ca}^{lj}	$\langle ki lb \rangle$	$t_k^c t_j^b$
-	λ_{ca}^{li}	$\langle kj lb \rangle$	$t_k^c t_j^b$
+	$\frac{1}{4}$	λ_{bc}^{jk}	$\langle li da \rangle t_{jkl}^{bcd}$
+	$\frac{1}{4}$	λ_{bc}^{ji}	$\langle kl da \rangle t_{jkl}^{bcd}$
+	$\frac{1}{4}$	λ_{ba}^{jk}	$\langle li cd \rangle t_{jkl}^{bcd}$
+	$\frac{1}{4}$	λ_{ba}^{ji}	$\langle kl cd \rangle t_{jkl}^{bcd}$
-	$\frac{1}{2}$	λ_{cd}^{kj}	$\langle li ba \rangle t_{kl}^{cd} t_j^b$
+	$\frac{1}{2}$	λ_{cd}^{ki}	$\langle lj ba \rangle t_{kl}^{cd} t_j^b$
+	$\frac{1}{4}$	λ_{cd}^{ji}	$\langle kl ba \rangle t_{kl}^{cd} t_j^b$
-	$\frac{1}{2}$	λ_{cb}^{kl}	$\langle ji da \rangle t_{kl}^{cd} t_j^b$
+	$\frac{1}{2}$	λ_{ca}^{kl}	$\langle ji db \rangle t_{kl}^{cd} t_j^b$
-		λ_{cb}^{ki}	$\langle lj da \rangle t_{kl}^{cd} t_j^b$
-		λ_{ca}^{kj}	$\langle li db \rangle t_{kl}^{cd} t_j^b$
+		λ_{ca}^{ki}	$\langle lj db \rangle t_{kl}^{cd} t_j^b$
+	$\frac{1}{2}$	λ_{ca}^{ji}	$\langle kl db \rangle t_{kl}^{cd} t_j^b$
+	$\frac{1}{4}$	λ_{ba}^{kl}	$\langle ji cd \rangle t_{kl}^{cd} t_j^b$
+	$\frac{1}{2}$	λ_{ba}^{ki}	$\langle lj cd \rangle t_{kl}^{cd} t_j^b$
+	$\frac{1}{2}$	λ_{dc}^{ji}	$\langle lk ba \rangle t_l^d t_k^c t_j^b$
+	$\frac{1}{2}$	λ_{da}^{kj}	$\langle li cb \rangle t_l^d t_k^c t_j^b$
-		λ_{da}^{ki}	$\langle lj cb \rangle t_l^d t_k^c t_j^b$
-	$\frac{1}{2}$	λ_{dba}^{jki}	$f_{dc} t_{j k}^{bc}$

Table 2--continued

+	$\frac{1}{2}$	λ_{bca}^{lji}	f_{kl}	t_{jk}^{bc}
+	$\frac{1}{4}$	λ_{deb}^{jki}	$\langle de ca \rangle$	t_{jk}^{bc}
+	$\frac{1}{8}$	λ_{dea}^{jki}	$\langle de bc \rangle$	t_{jk}^{bc}
+	$\frac{1}{4}$	λ_{bca}^{lmj}	$\langle ki lm \rangle$	t_{jk}^{bc}
+	$\frac{1}{8}$	λ_{bca}^{lmi}	$\langle jk lm \rangle$	t_{jk}^{bc}
-	$\frac{1}{2}$	λ_{dbc}^{lji}	$\langle kd al \rangle$	t_{jk}^{bc}
-	$\frac{1}{2}$	λ_{dba}^{ljk}	$\langle id cl \rangle$	t_{jk}^{bc}
+		λ_{dba}^{lji}	$\langle kd cl \rangle$	t_{jk}^{bc}
+	$\frac{1}{4}$	λ_{dea}^{kji}	$\langle de cb \rangle$	$t_k^c t_j^b$
+	$\frac{1}{4}$	λ_{cba}^{lmi}	$\langle kj lm \rangle$	$t_k^c t_j^b$
-		λ_{dca}^{lji}	$\langle kd bl \rangle$	$t_k^c t_j^b$
-	$\frac{1}{2}$	λ_{cda}^{kji}	$\langle cd bk \rangle$	t_j^b
+	$\frac{1}{2}$	λ_{cba}^{kli}	$\langle jc kl \rangle$	t_j^b
+	$\frac{1}{4}$	λ_{bca}^{jki}	$\langle bc jk \rangle$	
+	$\frac{1}{12}$	λ_{ebc}^{jkl}	$\langle ei da \rangle$	t_{jkl}^{bcd}
-	$\frac{1}{4}$	λ_{ebc}^{jki}	$\langle el da \rangle$	t_{jkl}^{bcd}
+	$\frac{1}{12}$	λ_{eba}^{jkl}	$\langle ei cd \rangle$	t_{jkl}^{bcd}
-	$\frac{1}{4}$	λ_{eba}^{jki}	$\langle el cd \rangle$	t_{jkl}^{bcd}
-	$\frac{1}{12}$	λ_{bcd}^{mjk}	$\langle li ma \rangle$	t_{jkl}^{bcd}
-	$\frac{1}{12}$	λ_{bcd}^{mji}	$\langle kl ma \rangle$	t_{jkl}^{bcd}
+	$\frac{1}{4}$	λ_{bca}^{mjk}	$\langle li md \rangle$	t_{jkl}^{bcd}

Table 2--continued

$$\begin{aligned}
& + \frac{1}{4} \lambda_{bca}^{mji} \langle kl || md \rangle t_{jkl}^{bcd} \\
& - \frac{1}{12} \lambda_{bcd}^{jki} f_{1a} t_{jkl}^{bcd} \\
& - \frac{1}{12} \lambda_{bca}^{jkl} f_{id} t_{jkl}^{bcd} \\
& + \frac{1}{4} \lambda_{bca}^{jki} f_{1d} t_{jkl}^{bcd} \\
& - \frac{1}{2} \lambda_{cda}^{kji} f_{1b} t_{kl}^{cd} t_j^b \\
& - \frac{1}{2} \lambda_{cba}^{kli} f_{jd} t_{kl}^{cd} t_j^b \\
& + \frac{1}{2} \lambda_{ecd}^{kji} \langle el || ba \rangle t_{kl}^{cd} t_j^b \\
& + \frac{1}{2} \lambda_{ecb}^{kli} \langle ej || da \rangle t_{kl}^{cd} t_j^b \\
& + \frac{1}{2} \lambda_{eca}^{klj} \langle ei || db \rangle t_{kl}^{cd} t_j^b \\
& - \frac{1}{2} \lambda_{eca}^{kli} \langle ej || db \rangle t_{kl}^{cd} t_j^b \\
& + \lambda_{eca}^{kji} \langle el || db \rangle t_{kl}^{cd} t_j^b \\
& - \frac{1}{4} \lambda_{eba}^{kli} \langle ej || cd \rangle t_{kl}^{cd} t_j^b \\
& - \frac{1}{2} \lambda_{cdb}^{mki} \langle lj || ma \rangle t_{kl}^{cd} t_j^b \\
& - \frac{1}{2} \lambda_{cda}^{mkj} \langle li || mb \rangle t_{kl}^{cd} t_j^b \\
& + \frac{1}{2} \lambda_{cda}^{mki} \langle lj || mb \rangle t_{kl}^{cd} t_j^b \\
& + \frac{1}{4} \lambda_{cda}^{mji} \langle kl || mb \rangle t_{kl}^{cd} t_j^b \\
& - \frac{1}{2} \lambda_{cba}^{mkl} \langle ji || md \rangle t_{kl}^{cd} t_j^b \\
& - \lambda_{cba}^{mki} \langle lj || md \rangle t_{kl}^{cd} t_j^b \\
& - \frac{1}{2} \lambda_{eda}^{kji} \langle el || cb \rangle t_1^d t_k^c t_j^b \\
& + \frac{1}{2} \lambda_{dca}^{mji} \langle lk || mb \rangle t_1^d t_k^c t_j^b \\
& - \frac{1}{12} \lambda_{cde}^{klj} \langle mi || ba \rangle t_{klm}^{cde} t_j^b
\end{aligned}$$

Table 2--continued

$+ \frac{1}{12}$	λ_{cde}^{kli}	$\langle mj ba \rangle$	$t_{klm}^{cde} t_j^b$
$+ \frac{1}{12}$	λ_{cde}^{kji}	$\langle lm ba \rangle$	$t_{klm}^{cde} t_j^b$
$- \frac{1}{12}$	λ_{cdb}^{klm}	$\langle ji ea \rangle$	$t_{klm}^{cde} t_j^b$
$+ \frac{1}{12}$	λ_{cda}^{klm}	$\langle ji eb \rangle$	$t_{klm}^{cde} t_j^b$
$- \frac{1}{4}$	λ_{cdb}^{kli}	$\langle mj ea \rangle$	$t_{klm}^{cde} t_j^b$
$- \frac{1}{4}$	λ_{cda}^{klj}	$\langle mi eb \rangle$	$t_{klm}^{cde} t_j^b$
$+ \frac{1}{4}$	λ_{cda}^{kli}	$\langle mj eb \rangle$	$t_{klm}^{cde} t_j^b$
$+ \frac{1}{4}$	λ_{cda}^{kji}	$\langle lm eb \rangle$	$t_{klm}^{cde} t_j^b$
$+ \frac{1}{12}$	λ_{cba}^{klm}	$\langle ji de \rangle$	$t_{klm}^{cde} t_j^b$
$+ \frac{1}{4}$	λ_{cba}^{kli}	$\langle mj de \rangle$	$t_{klm}^{cde} t_j^b$
$+ \frac{1}{4}$	λ_{deb}^{ljk}	$\langle mi ca \rangle$	$t_{lm}^{de} t_{jk}^{bc}$
$- \frac{1}{2}$	λ_{deb}^{lji}	$\langle mk ca \rangle$	$t_{lm}^{de} t_{jk}^{bc}$
$+ \frac{1}{8}$	λ_{dea}^{ljk}	$\langle mi bc \rangle$	$t_{lm}^{de} t_{jk}^{bc}$
$- \frac{1}{4}$	λ_{dea}^{lji}	$\langle mk bc \rangle$	$t_{lm}^{de} t_{jk}^{bc}$
$+ \frac{1}{8}$	λ_{deb}^{jki}	$\langle lm ca \rangle$	$t_{lm}^{de} t_{jk}^{bc}$
$+ \frac{1}{16}$	λ_{dea}^{jki}	$\langle lm bc \rangle$	$t_{lm}^{de} t_{jk}^{bc}$
$- \frac{1}{2}$	λ_{dba}^{lmj}	$\langle ki ec \rangle$	$t_{lm}^{de} t_{jk}^{bc}$
$- \frac{1}{4}$	λ_{dba}^{lmi}	$\langle jk ec \rangle$	$t_{lm}^{de} t_{jk}^{bc}$
$+ \frac{1}{2}$	λ_{dba}^{lji}	$\langle mk ec \rangle$	$t_{lm}^{de} t_{jk}^{bc}$
$+ \frac{1}{2}$	λ_{dec}^{lji}	$\langle mk ba \rangle$	$t_{lm}^{de} t_k^c t_j^b$
$+ \frac{1}{4}$	λ_{dea}^{lkj}	$\langle mi cb \rangle$	$t_{lm}^{de} t_k^c t_j^b$

Table 2--continued

$$\begin{aligned}
& - \frac{1}{2} \lambda_{dea}^{lki} \langle mj || cb \rangle t_{lm}^{de} t_k^c t_j^b \\
& + \frac{1}{8} \lambda_{dea}^{kji} \langle lm || cb \rangle t_{lm}^{de} t_k^c t_j^b \\
& + \frac{1}{4} \lambda_{dcb}^{lmi} \langle kj || ea \rangle t_{lm}^{de} t_k^c t_j^b \\
& + \frac{1}{2} \lambda_{dca}^{lmj} \langle ki || eb \rangle t_{lm}^{de} t_k^c t_j^b \\
& - \frac{1}{2} \lambda_{dca}^{lmi} \langle kj || eb \rangle t_{lm}^{de} t_k^c t_j^b \\
& - \lambda_{dca}^{lji} \langle mk || eb \rangle t_{lm}^{de} t_k^c t_j^b \\
& + \frac{1}{8} \lambda_{cba}^{lmi} \langle kj || de \rangle t_{lm}^{de} t_k^c t_j^b \\
& + \frac{1}{4} \lambda_{eda}^{kji} \langle ml || cb \rangle t_m^e t_l^d t_k^c t_j^b
\end{aligned}$$

Note: Summation over all but the target labels i and a is implied.

Table 3. The Λ_2 Equation for the CCSDT Derivative Model.

$$\begin{aligned}
0 = & \langle ij || ab \rangle + P(ij|ab) \lambda_a^i f_{jb} \\
& + P(ij|ab) \lambda_a^i \langle kj || cb \rangle t_k^c \\
& + P(ij) \lambda_c^i \langle cj || ab \rangle \\
& - P(ab) \lambda_a^k \langle ij || kb \rangle \\
& - P(ij) \lambda_c^i \langle kj || ab \rangle t_k^c \\
& - P(ab) \lambda_a^k \langle ij || cb \rangle t_k^c \\
& + P(ij) \lambda_{ab}^{ki} f_{jk} \\
& - P(ab) \lambda_{ca}^{ij} f_{cb} \\
& + \frac{1}{2} \lambda_{cd}^{ij} \langle cd || ab \rangle \\
& + \frac{1}{2} \lambda_{ab}^{kl} \langle ij || kl \rangle \\
& + P(ab|ij) \lambda_{ca}^{ki} \langle jc || bk \rangle \\
& + P(ab) \lambda_{ca}^{ij} f_{kb} t_k^c \\
& + P(ij) \lambda_{ab}^{ki} f_{jc} t_k^c \\
& - \lambda_{dc}^{ij} \langle dk || ab \rangle t_k^c \\
& + P(ab|ij) \lambda_{da}^{ki} \langle dj || cb \rangle t_k^c \\
& + P(ab) \lambda_{da}^{ij} \langle dk || cb \rangle t_k^c \\
& - P(ab|ij) \lambda_{ca}^{li} \langle kj || lb \rangle t_k^c \\
& + \lambda_{ab}^{lk} \langle ij || lc \rangle t_k^c \\
& - P(ij) \lambda_{ab}^{li} \langle kj || lc \rangle t_k^c \\
& - \frac{1}{2} P(ij) \lambda_{cd}^{ki} \langle lj || ab \rangle t_{kl}^{cd} \\
& + \frac{1}{4} \lambda_{cd}^{ij} \langle kl || ab \rangle t_{kl}^{cd}
\end{aligned}$$

Table 3--continued

- $\frac{1}{2} P(ab)$	$\lambda_{ca}^{kl} \langle ij db \rangle$	t_{kl}^{cd}
+ $P(ab ij)$	$\lambda_{ca}^{ki} \langle lj db \rangle$	t_{kl}^{cd}
- $\frac{1}{2} P(ab)$	$\lambda_{ca}^{ij} \langle kl db \rangle$	t_{kl}^{cd}
+ $\frac{1}{4}$	$\lambda_{ab}^{kl} \langle ij cd \rangle$	t_{kl}^{cd}
- $\frac{1}{2} P(ij)$	$\lambda_{ab}^{ki} \langle lj cd \rangle$	t_{kl}^{cd}
+ $\frac{1}{2}$	$\lambda_{dc}^{ij} \langle lk ab \rangle$	$t_1^d t_k^c$
- $P(ab ij)$	$\lambda_{da}^{ki} \langle lj cb \rangle$	$t_1^d t_k^c$
- $P(ab)$	$\lambda_{da}^{ij} \langle lk cb \rangle$	$t_1^d t_k^c$
+ $\frac{1}{2}$	$\lambda_{ab}^{lk} \langle ij dc \rangle$	$t_1^d t_k^c$
- $P(ij)$	$\lambda_{ab}^{li} \langle kj dc \rangle$	$t_1^d t_k^c$
+	$\lambda_{cab}^{kij} f_{ck}$	
+ $\frac{1}{2} P(ab)$	$\lambda_{cda}^{kij} \langle cd bk \rangle$	
- $\frac{1}{2} P(ij)$	$\lambda_{cab}^{kli} \langle jc kl \rangle$	
-	$\lambda_{cab}^{lij} f_{kl} t_k^c$	
+	$\lambda_{dab}^{kij} f_{dc} t_k^c$	
- $\frac{1}{2} P(ab)$	$\lambda_{dea}^{kij} \langle de cb \rangle$	t_k^c
- $\frac{1}{2} P(ij)$	$\lambda_{cab}^{lmi} \langle kj lm \rangle$	t_k^c
+ $P(ab)$	$\lambda_{dca}^{lij} \langle kd bl \rangle$	t_k^c
+ $P(ij)$	$\lambda_{dab}^{lki} \langle jd cl \rangle$	t_k^c
+	$\lambda_{dab}^{lij} \langle kd cl \rangle$	t_k^c
+ $\frac{1}{2} P(ab)$	$\lambda_{cda}^{kij} f_{1b} t_{kl}^{cd}$	

Table 3--continued

$+$	$\frac{1}{2} P(ij)$	$\lambda_{cab}^{kli} f_{jd} t_{kl}^{cd}$
$+$		$\lambda_{cab}^{kij} f_{ld} t_{kl}^{cd}$
$+$	$\frac{1}{2}$	$\lambda_{ecd}^{kij} \langle e1 ab \rangle t_{kl}^{cd}$
$-$	$\frac{1}{2} P(ab ij)$	$\lambda_{eca}^{kli} \langle ej db \rangle t_{kl}^{cd}$
$-$	$P(ab)$	$\lambda_{eca}^{kij} \langle e1 db \rangle t_{kl}^{cd}$
$+$	$\frac{1}{4} P(ij)$	$\lambda_{eab}^{kli} \langle ej cd \rangle t_{kl}^{cd}$
$+$	$\frac{1}{2}$	$\lambda_{eab}^{kij} \langle e1 cd \rangle t_{kl}^{cd}$
$+$	$\frac{1}{2} P(ab ij)$	$\lambda_{cda}^{mki} \langle lj mb \rangle t_{kl}^{cd}$
$-$	$\frac{1}{4} P(ab)$	$\lambda_{cda}^{mij} \langle kl mb \rangle t_{kl}^{cd}$
$-$	$\frac{1}{2}$	$\lambda_{cab}^{mkl} \langle ij md \rangle t_{kl}^{cd}$
$+$	$P(ij)$	$\lambda_{cab}^{mki} \langle lj md \rangle t_{kl}^{cd}$
$-$	$\frac{1}{2}$	$\lambda_{cab}^{mij} \langle kl md \rangle t_{kl}^{cd}$
$+$	$P(ab)$	$\lambda_{eda}^{kij} \langle e1 cb \rangle t_1^d t_k^c$
$+$	$\frac{1}{2} P(ij)$	$\lambda_{eab}^{lki} \langle ej dc \rangle t_1^d t_k^c$
$+$		$\lambda_{eab}^{lij} \langle ek dc \rangle t_1^d t_k^c$
$-$	$\frac{1}{2} P(ab)$	$\lambda_{dca}^{mij} \langle lk mb \rangle t_1^d t_k^c$
$-$	$P(ij)$	$\lambda_{dab}^{mki} \langle lj mc \rangle t_1^d t_k^c$
$-$		$\lambda_{dab}^{mij} \langle lk mc \rangle t_1^d t_k^c$
$-$	$\frac{1}{12} P(ij)$	$\lambda_{cde}^{kli} \langle mj ab \rangle t_{klm}^{cde}$
$+$	$\frac{1}{12}$	$\lambda_{cde}^{kij} \langle lm ab \rangle t_{klm}^{cde}$
$-$	$\frac{1}{12} P(ab)$	$\lambda_{cda}^{klm} \langle ij eb \rangle t_{klm}^{cde}$

Table 3--continued

$+$	$\frac{1}{4} P(ab ij)$	$\lambda_{cda}^{kli} \langle mj eb \rangle$	t_{klm}^{cde}
$-$	$\frac{1}{4} P(ab)$	$\lambda_{cda}^{kij} \langle lm eb \rangle$	t_{klm}^{cde}
$+$	$\frac{1}{12}$	$\lambda_{cab}^{klm} \langle ij de \rangle$	t_{klm}^{cde}
$-$	$\frac{1}{4} P(ij)$	$\lambda_{cab}^{kli} \langle mj de \rangle$	t_{klm}^{cde}
$+$	$\frac{1}{4}$	$\lambda_{cab}^{kij} \langle lm de \rangle$	t_{klm}^{cde}
$+$	$\frac{1}{2}$	$\lambda_{dec}^{lij} \langle mk ab \rangle$	$t_{lm}^{de} t_k^c$
$-$	$\frac{1}{2} P(ab ij)$	$\lambda_{dea}^{lki} \langle mj cb \rangle$	$t_{lm}^{de} t_k^c$
$-$	$\frac{1}{2} P(ab)$	$\lambda_{dea}^{lij} \langle mk cb \rangle$	$t_{lm}^{de} t_k^c$
$-$	$\frac{1}{4} P(ab)$	$\lambda_{dea}^{kij} \langle lm cb \rangle$	$t_{lm}^{de} t_k^c$
$-$	$\frac{1}{2} P(ab ij)$	$\lambda_{dca}^{lmi} \langle kj eb \rangle$	$t_{lm}^{de} t_k^c$
$+$	$\frac{1}{2}$	$\lambda_{dab}^{lmk} \langle ij ec \rangle$	$t_{lm}^{de} t_k^c$
$-$	$\frac{1}{2} P(ij)$	$\lambda_{dab}^{lmi} \langle kj ec \rangle$	$t_{lm}^{de} t_k^c$
$+$	$P(ab)$	$\lambda_{dca}^{lij} \langle mk eb \rangle$	$t_{lm}^{de} t_k^c$
$+$	$P(ij)$	$\lambda_{dab}^{lki} \langle mj ec \rangle$	$t_{lm}^{de} t_k^c$
$+$		$\lambda_{dab}^{lij} \langle mk ec \rangle$	$t_{lm}^{de} t_k^c$
$+$	$\frac{1}{2}$	$\lambda_{dab}^{kij} \langle lm ec \rangle$	$t_{lm}^{de} t_k^c$
$-$	$\frac{1}{4} P(ij)$	$\lambda_{cab}^{lmi} \langle kj de \rangle$	$t_{lm}^{de} t_k^c$
$+$	$\frac{1}{2}$	$\lambda_{cab}^{lij} \langle mk de \rangle$	$t_{lm}^{de} t_k^c$
$-$	$\frac{1}{2} P(ab)$	$\lambda_{eda}^{kij} \langle ml cb \rangle$	$t_m^e t_1^d t_k^c$
$-$	$\frac{1}{2} P(ij)$	$\lambda_{eab}^{lki} \langle mj dc \rangle$	$t_m^e t_1^d t_k^c$
$-$		$\lambda_{eab}^{lij} \langle mk dc \rangle$	$t_m^e t_1^d t_k^c$

Note: Summation over all but the target labels i, j, a and b is implied.

$P(pq)$ is an operator that generates two terms:

$P(pq) = \text{identity} - \text{interchange } p \leftrightarrow q.$

$P(ab|ij)$ is an operator that generates four terms:

$P(ab|ij) = \text{identity} - \text{interchange } a \leftrightarrow b - \text{interchange } i \leftrightarrow j$
 $+ \text{interchange both } a \leftrightarrow b \text{ and } i \leftrightarrow j.$

Table 4. The Λ_3 Equation for the CCSDT Derivative Model.

$$\begin{aligned}
0 = & P(c/ab|k/ij) \langle ij || ab \rangle \lambda_c^k \\
& + P(c/ab|k/ij) \lambda_{ab}^{ij} \langle lk || dc \rangle t_1^d \\
& + P(c/ab|k/ij) \lambda_{ab}^{ij} f_{kc} \\
& - P(a/bc|k/ij) \lambda_{da}^{ij} \langle dk || bc \rangle \\
& + P(c/ab|i/jk) \lambda_{ab}^{li} \langle jk || lc \rangle \\
& + P(a/bc|k/ij) \lambda_{da}^{ij} \langle lk || bc \rangle t_1^d \\
& + P(c/ab|i/jk) \lambda_{ab}^{li} \langle jk || dc \rangle t_1^d \\
& - P(k/ij) \lambda_{abc}^{lij} f_{kl} \\
& + P(c/ab) \lambda_{dab}^{ijk} f_{dc} \\
& + \frac{1}{2} P(a/bc) \lambda_{dea}^{ijk} \langle de || bc \rangle \\
& + \frac{1}{2} P(i/jk) \lambda_{abc}^{lmi} \langle jk || lm \rangle \\
& + P(c/ab|k/ij) \lambda_{dab}^{lij} \langle kd || cl \rangle \\
& - P(c/ab) \lambda_{dab}^{ijk} f_{lc} t_1^d \\
& - P(k/ij) \lambda_{abc}^{lij} f_{kd} t_1^d \\
& - P(a/bc) \lambda_{eda}^{ijk} \langle el || bc \rangle t_1^d \\
& + P(c/ab|k/ij) \lambda_{eab}^{lij} \langle ek || dc \rangle t_1^d \\
& - P(c/ab) \lambda_{eab}^{ijk} \langle el || dc \rangle t_1^d \\
& - P(c/ab|k/ij) \lambda_{dab}^{mij} \langle lk || mc \rangle t_1^d \\
& + P(i/jk) \lambda_{abc}^{mli} \langle jk || md \rangle t_1^d \\
& + P(k/ij) \lambda_{abc}^{mij} \langle lk || md \rangle t_1^d \\
& + \frac{1}{2} P(a/bc|k/ij) \lambda_{dea}^{lij} \langle mk || bc \rangle t_{lm}^{de}
\end{aligned}$$

Table 4--continued

+	$\frac{1}{4}$	$P(a/bc)$	λ_{dea}^{ijk}	$\langle lm bc \rangle$	t_{lm}^{de}
+	$\frac{1}{2}$	$P(c/ab i/jk)$	λ_{dab}^{lmi}	$\langle jk ec \rangle$	t_{lm}^{de}
+		$P(c/ab k/ij)$	λ_{dab}^{lij}	$\langle mk ec \rangle$	t_{lm}^{de}
+	$\frac{1}{2}$	$P(c/ab)$	λ_{dab}^{ijk}	$\langle lm ec \rangle$	t_{lm}^{de}
+	$\frac{1}{4}$	$P(i/jk)$	λ_{abc}^{lmi}	$\langle jk de \rangle$	t_{lm}^{de}
+	$\frac{1}{2}$	$P(k/ij)$	λ_{abc}^{lij}	$\langle mk de \rangle$	t_{lm}^{de}
+	$\frac{1}{2}$	$P(a/bc)$	λ_{eda}^{ijk}	$\langle ml bc \rangle$	$t_m^e t_l^d$
-		$P(c/ab k/ij)$	λ_{eab}^{lij}	$\langle mk dc \rangle$	$t_m^e t_l^d$
+		$P(c/ab)$	λ_{eab}^{ijk}	$\langle ml dc \rangle$	$t_m^e t_l^d$
+	$\frac{1}{2}$	$P(i/jk)$	λ_{abc}^{mli}	$\langle jk ed \rangle$	$t_m^e t_l^d$
+		$P(k/ij)$	λ_{abc}^{mij}	$\langle lk ed \rangle$	$t_m^e t_l^d$

Note: Summation over all but the target labels i, j, k, a, b and c is implied.

$P(p/qr)$ is an operator that generates three terms:

$P(p/qr)$ = identity - interchange $p \leftrightarrow q$ - interchange $p \leftrightarrow r$.

$P(a/bc|i/jk)$ is an operator that generates nine terms:

$P(a/bc|i/jk)$ = identity - interchange $a \leftrightarrow b$ - interchange $a \leftrightarrow c$
 - interchange $i \leftrightarrow j$ - interchange $i \leftrightarrow k$

+ interchange both $a \leftrightarrow b$ and $i \leftrightarrow j$ + interchange both $a \leftrightarrow b$ and $i \leftrightarrow k$

+ interchange both $a \leftrightarrow c$ and $i \leftrightarrow j$ + interchange both $a \leftrightarrow c$ and $i \leftrightarrow k$.

Expressions for the Choice of SCF Reference

For canonical SCF orbitals, all terms in Table (1) involving the derivative integrals of f_N^X vanish, except for those involving the diagonal elements $f_{ii}^X = \epsilon_i^X$ and $f_{aa}^X = \epsilon_a^X$ —the derivative SCF eigenvalues. The results of CPHF theory¹⁵ are now summarized for canonical SCF orbitals $\{\phi(X)\}$ expanded in a primitive AO basis set $\{\psi(X)\}$.

In this section, all orbitals are assumed to be unperturbed; i.e. evaluated at $X=0$, unless otherwise shown as a function of X . Derivative orbitals, evaluated at $X=0$, are indicated by the superscript X .

$$\begin{aligned} |p(X)\rangle &= \phi_p(X) & |p\rangle &= |p(X)\rangle|_{X=0} & |p^X\rangle &= \left. \frac{\partial |p(X)\rangle}{\partial X} \right|_{X=0} \\ |\mu(X)\rangle &= \psi_\mu(X) & |\mu\rangle &= |\mu(X)\rangle|_{X=0} & |\mu^X\rangle &= \left. \frac{\partial |\mu(X)\rangle}{\partial X} \right|_{X=0} \end{aligned}$$

As usual, the labels a, b, \dots and i, j, \dots are used to represent the SCF virtual orbitals and occupied orbitals, respectively, while p, q, r, \dots are unrestricted. The labels $\mu, \nu, \lambda, \sigma, \dots$ are used to represent the primitive AO basis functions. The derivative of an SCF orbital, evaluated at $X=0$, is given by a linear combination of unperturbed SCF orbitals and a term arising from the derivative of the primitive AO basis functions:

$$|a^X\rangle = \sum_{f \neq a} U_{fa}^X |f\rangle + \sum_k U_{ka}^X |k\rangle + \sum_\mu C_{\mu a} |\mu^X\rangle \quad (19)$$

$$|i^X\rangle = \sum_f U_{fi}^X |f\rangle + \sum_{k \neq i} U_{ki}^X |k\rangle + \sum_\mu C_{\mu i} |\mu^X\rangle \quad (20)$$

The SCF coefficients for the unperturbed molecular orbital p are given by $C_{\mu p}$. The coefficients U_{pq}^X are called the CPHF coefficients. The virtual-occupied block of the CPHF coefficients are determined by solving the linear equation:

$$U_{ai}^X = \sum_{bj} (A^{-1})_{ai,bj} \frac{Q_{bj}^X}{\epsilon_j - \epsilon_b}, \quad (21)$$

where

$$A_{ai,bj} = 1 + \frac{\langle ab || ij \rangle + \langle aj || ib \rangle}{\epsilon_a - \epsilon_i}$$

and ϵ_p is the unperturbed orbital eigenvalue of orbital p . Once the virtual-occupied block is determined, the occupied-occupied and virtual-virtual blocks are then determined as well:

$$U_{ki}^X = \frac{-1}{(\epsilon_k - \epsilon_i)} [Q_{ki}^X + \sum_{g,m} U_{gm}^X (\langle km || ig \rangle + \langle kg || im \rangle)] \quad (22)$$

$$U_{fa}^X = \frac{-1}{(\epsilon_f - \epsilon_a)} [Q_{fa}^X + \sum_{g,m} U_{gm}^X (\langle fm || ag \rangle + \langle fg || am \rangle)] . \quad (23)$$

The occupied-virtual CPHF coefficients are determined by the derivative of the SCF orthonormality condition:

$$U_{pq}^X + (U_{qp}^X)^* + S_{pq}^X = 0 . \quad (24)$$

The elements of the general one-electron perturbation matrix Q^X are given by:

$$Q_{pq}^X = h_{pq}^X - S_{pq}^X \zeta_{pq} - \sum_{k,l} S_{kl}^X \langle pl || qk \rangle + \sum_{\substack{\mu, \nu \\ \lambda, \sigma}} (C_{\mu p})^* C_{\nu q} P_{\lambda \sigma} \left. \frac{\partial \langle \mu \lambda || \nu \sigma \rangle}{\partial X} \right|_{X=0}, \quad (25)$$

where

$$\zeta_{pq} = \begin{cases} \frac{1}{2} (\epsilon_p + \epsilon_q) & \text{when } p \text{ and } q \text{ are both} \\ & \text{virtual or both occupied} \\ \epsilon_q & \text{otherwise} \end{cases} .$$

The symbol $P_{\lambda\sigma}$ represents an element of the SCF density matrix in the AO basis. The matrix h_{pq}^X consists of the derivative of the matrix elements of the one-electron part of the Hamiltonian in the primitive, perturbation-dependent basis $\{\psi(X)\}$, but transformed into the unperturbed orbital basis $\{\phi\}$.

$$h_{pq}^X = \sum_{\mu, \nu} (C_{\mu p})^* C_{\nu q} \left. \frac{\partial \langle \mu(X) | h(X) | \nu(X) \rangle}{\partial X} \right|_{X=0}$$

Similarly, the matrix S_{pq}^X is the derivative of the overlap matrix of the perturbation-dependent primitive basis functions, transformed into the unperturbed orbital basis.

$$S_{pq}^X = \sum_{\mu, \nu} (C_{\mu p})^* C_{\nu q} \left. \frac{\partial \langle \mu(X) | \nu(X) \rangle}{\partial X} \right|_{X=0} \quad (26)$$

For a uniform external field perturbation in the z-direction, the elements of the perturbation matrix Q are simply:

$$Q_{pq}^X = h_{pq}^X = \langle p | z | q \rangle .$$

For the delta-function perturbation³⁶ located at the point r, we have:

$$Q_{pq}^X = h_{pq}^X = \langle p | \delta(r' - r) | q \rangle = \phi_p^*(r) \phi_q(r) . \quad (27)$$

The derivative of the SCF orbital eigenvalues, the diagonal elements of the Fock matrix, are given by:

$$\begin{aligned} \epsilon_a^X &= Q_{aa}^X + \sum_{g,m} U_{gm}^X (\langle am | ag \rangle + \langle ag | am \rangle) \\ \epsilon_i^X &= Q_{ii}^X + \sum_{g,m} U_{gm}^X (\langle im | ig \rangle + \langle ig | im \rangle) . \end{aligned}$$

Now we could use the above identities to develop the expression for $\Delta \epsilon^X$, except that the occupied-occupied and virtual-virtual CPBF

coefficients (Equations (22) and (23)) possess denominators involving the difference of unperturbed occupied or virtual eigenvalues. Such denominators must be eliminated by subsequent factorization of the derivative energy expression; otherwise the expression will not be applicable to molecular systems with degeneracies or near degeneracies. Since CC theory and its finite-order MBPT approximations are invariant under unitary transformations so long as occupied and virtual orbitals are not mixed, we may make a particular choice of non-canonical SCF orbitals to simplify the derivative expressions without loss of generality. Rather than introduce singularities which must be later eliminated, we follow the development of Handy et al. for MBPT(2) gradients²⁹ by choosing non-canonical SCF orbitals such that:

$$U_{fa}^X = -\frac{1}{2} S_{fa}^X |f\rangle \quad (28)$$

$$U_{ki}^X = -\frac{1}{2} S_{ki}^X |k\rangle, \quad (29)$$

as found in early studies by Moccia³⁷ and Pulay.¹⁵ The problematic denominators of the occupied-occupied and virtual-virtual CPHF coefficients for canonical orbitals are not present; the virtual-occupied CPHF coefficients are determined as in Equation (21). For the choice of non-canonical orbitals, however, the off-diagonal elements f_{ab}^X and f_{ij}^X are not zero. These matrix elements are given by:

$$f_{ab}^X = Q_{ab}^X + \sum_{g,m} U_{gm}^X (\langle am || bg \rangle + \langle ag || bm \rangle) \quad (30)$$

$$f_{ij}^X = Q_{ij}^X + \sum_{g,m} U_{gm}^X (\langle im || jg \rangle + \langle ig || jm \rangle). \quad (31)$$

Equations (28-31) and Equation (24) are to be applied to the CCSDT energy derivative expression given in Table (1). First, gathering together the common derivative two-electron integrals and the non-zero derivative Fock matrix elements, we define the intermediates Γ and D for a more compact expression:

$$\begin{aligned} \Delta E^X = & D_{ij} f_{ij}^X + D_{ab} f_{ab}^X \\ & + \Gamma(ij,ab) \langle ij || ab \rangle^X + \Gamma(ab,cd) \langle ab || cd \rangle^X \\ & + \Gamma(kl,ij) \langle kl || ij \rangle^X + \Gamma(ja,bi) \langle ja || bi \rangle^X \\ & + \Gamma(ai,bc) \langle ai || bc \rangle^X + \Gamma(jk,ia) \langle jk || ia \rangle^X, \end{aligned}$$

where summation over all labels is implied. The D and Γ intermediates for the CCSDT model are defined in Tables (5) and (6), respectively. For the CCSDT-1 model, the contributions to the Γ 's which arise from terms [2-27], [2-28] and [2-29] are excluded. In addition, the contributions from terms involving Λ_3 are excluded, with the exception of terms [3-1], [3-2], [3-8] and [3-9]. We will show that the D intermediates so defined are the occupied-occupied and virtual-virtual blocks of the density matrix.

Now, using the identities from CPHF theory, we expand the derivative integrals, and obtain the following:

$$\begin{aligned} \Delta E^X = & D_{ij} (Q_{ij}^X + U_{em}^X (\langle ie || jm \rangle + \langle im || je \rangle)) \\ & + D_{ab} (Q_{ab}^X + U_{em}^X (\langle ae || bm \rangle + \langle am || be \rangle)) \\ & + (\Gamma(ij,ab) - \Gamma(ji,ab)) (U_{ei}^X \langle ej || ab \rangle - 1/2 S_{mi}^X \langle mj || ab \rangle) \end{aligned} \quad (32)$$

$$\begin{aligned}
& + (\Gamma(ij,ab) - \Gamma(ij,ba)) ([-U_{am}^X - S_{am}^X] \langle ij || mb \rangle - 1/2 S_{ea}^X \langle ij || eb \rangle) \\
& + (\Gamma(ab,cd) - \Gamma(ba,cd) + \Gamma(cd,ab) - \Gamma(cd,ba)) \\
& \quad \times ([-U_{am}^X - S_{am}^X] \langle mb || cd \rangle - 1/2 S_{ea}^X \langle eb || cd \rangle) \\
& + (\Gamma(kl,ij) - \Gamma(lk,ij) + \Gamma(ij,kl) - \Gamma(ij,lk)) \\
& \quad \times (U_{ek}^X \langle el || ij \rangle - 1/2 S_{mk}^X \langle ml || ij \rangle) \\
& + (\Gamma(ja,bi) + \Gamma(ib,aj)) (U_{ej}^X \langle ea || bi \rangle - 1/2 S_{mj}^X \langle ma || bi \rangle) \\
& + (\Gamma(ja,bi) + \Gamma(ib,aj)) ([-U_{am}^X - S_{am}^X] \langle jm || bi \rangle - 1/2 S_{ea}^X \langle je || bi \rangle) \\
& + \Gamma(ai,bc) ([-U_{am}^X - S_{am}^X] \langle mi || bc \rangle - 1/2 S_{ea}^X \langle ei || bc \rangle) \\
& + \Gamma(ai,bc) (U_{ei}^X \langle ae || bc \rangle - 1/2 S_{mi}^X \langle am || bc \rangle) \\
& + (\Gamma(ai,bc) - \Gamma(ai,cb)) ([-U_{bm}^X - S_{bm}^X] \langle ai || mc \rangle - 1/2 S_{eb}^X \langle ai || ec \rangle) \\
& + (\Gamma(jk,ia) - \Gamma(kj,ia)) (U_{ej}^X \langle ek || ia \rangle - 1/2 S_{mj}^X \langle mk || ia \rangle) \\
& + \Gamma(jk,ia) (U_{ei}^X \langle jk || ea \rangle - 1/2 S_{mi}^X \langle jk || ma \rangle) \\
& + \Gamma(jk,ia) ([-U_{am}^X - S_{am}^X] \langle jk || im \rangle - 1/2 S_{ea}^X \langle jk || ie \rangle) \\
& + \text{A0 derivative part} .
\end{aligned}$$

Contributions arising from the derivative of the primitive A0 basis functions when Equations (19) and (20) are applied to the derivative two-electron integrals are called the "A0 derivative part". The A0 derivative part is not explicitly shown here because the following discussion is concerned with manipulations of the other terms. Rather, the A0 derivative part is shown in final, computational form in Table (7). In Table (7), we follow Fitzgerald et al.²⁶ and define

a perturbation-independent quantity $\Gamma(\mu\nu\rho\sigma)$ by the application of MO-to-AO transformations to the Γ intermediates. The transformation of 3N sets of derivative integrals to the MO basis is thereby avoided. Instead, only the one transformation in the construction of the perturbation-independent $\Gamma(\mu\nu\rho\sigma)$ is necessary. The AO derivative part of each of the 3N gradients is computed by the dot-product of $\Gamma(\mu\nu\rho\sigma)$ with the AO derivative integrals as they are generated for each of the 3N degrees of freedom.

We gather together the common terms of Equation (32) by defining computational intermediates I and X such that:

$$\begin{aligned} \Delta E^X = & \sum_{i,j} D_{ij} Q_{ij}^X + \sum_{a,b} D_{ab} Q_{ab}^X + 2 \sum_{a,i} X_{ai} U_{ai}^X \\ & + \sum_{i,j} I_{ij} S_{ij}^X + \sum_{a,b} I_{ab} S_{ab}^X + 2 \sum_{a,i} I_{ai} S_{ai}^X \\ & + \text{AO derivative part} \end{aligned}$$

The intermediates X and I are summarized in Table (8). Now recall that the CPHF coefficients are the solutions to a linear equation. Hence, we use the Z-vector method^{22,34} to eliminate the CPHF coefficients from the expression:

$$2 \sum_{a,i} X_{ai} U_{ai}^X = 2 \sum_{ai} X_{ai} \sum_{bj} (A^{-1})_{ai,bj} \frac{Q_{bj}^X}{\epsilon_j - \epsilon_b} = 2 \sum_{b,j} D_{bj} Q_{bj}^X,$$

where the summation over the labels a and i has been carried out in the term at the far right. The virtual-occupied block of the matrix D_{bj} is the solution to the perturbation-independent linear equation:

$$\sum_{bj} D_{bj} (\epsilon_j - \epsilon_b) A_{bj,ai} = X_{ai}. \quad (33)$$

Finally we have the computational form of the energy derivative:

$$\begin{aligned} \Delta E^X = & \sum_{i,j} D_{ij} Q_{ij}^X + \sum_{a,b} D_{ab} Q_{ab}^X + 2 \sum_{a,i} D_{ai} Q_{ai}^X \\ & + \sum_{i,j} I_{ij} S_{ij}^X + \sum_{a,b} I_{ab} S_{ab}^X + 2 \sum_{a,i} I_{ai} S_{ai}^X \\ & + \text{AO derivative part} . \end{aligned} \quad (34)$$

In the special case of the applied external field, Equation (34) reduces to

$$\Delta E^X = \sum_{p,q} D_{pq} Q_{pq}^X .$$

Thus, for the delta-function perturbation (see Equation (27)) we have

$$\Delta E^X = \sum_{p,q} D_{pq} \phi_p^*(r) \phi_q(r) ,$$

and we identify the matrix D as the matrix representation of the correlation correction to the electron density. When added to the SCF density matrix, the total response density matrix is obtained. Since the molecular orbitals are allowed to "relax" in the presence of the perturbation, the response density necessarily contains all orbital relaxation effects, as opposed to a density constructed by taking the expectation value over a given unperturbed wavefunction. It is well known that iteration of the CPHF equation (Equation (21)) and subsequent substitution into the SCF second derivative energy expression yields certain classes of double-perturbation diagrams to all orders.³⁵ Similarly the first derivative of the MBPT/CC energy is actually an infinite sum of diagrams in double perturbation theory.³⁹

Table 5. The Occupied-Occupied and Virtual-Virtual Blocks of the CCSDT Density Matrix.

$$D_{ij} = - \lambda_a^j t_i^a + \frac{1}{2} \lambda_{ab}^{jk} t_{ki}^{ab} - \frac{1}{12} \lambda_{abc}^{jlk} t_{lki}^{abc}$$

$$D_{ab} = \lambda_a^i t_i^b - \frac{1}{2} \lambda_{ac}^{ij} t_{ij}^{cb} + \frac{1}{12} \lambda_{adc}^{ijk} t_{ijk}^{dcb}$$

Note: Summation over all but target labels is implied.

Table 6. The Γ Intermediates.

$$\begin{aligned}
\Gamma(ij,ab) = & \frac{1}{4} \lambda_{ab}^{ij} \\
& + \frac{1}{4} t_{ij}^{ab} \\
& + \frac{1}{2} t_i^a t_j^b \\
& + \frac{1}{4} \lambda_c^k t_{kij}^{cab} \\
& + \lambda_c^k t_{ki}^{ca} t_j^b \\
& + \frac{1}{2} \lambda_c^k t_{ij}^{ca} t_k^b \\
& + \frac{1}{2} \lambda_c^k t_{ki}^{ab} t_j^c \\
& + \lambda_c^k t_k^a t_i^b t_j^c \\
& + \frac{1}{4} \lambda_{dc}^{lk} t_{lki}^{dca} t_j^b \\
& + \frac{1}{4} \lambda_{dc}^{lk} t_{lij}^{dca} t_k^b \\
& + \frac{1}{4} \lambda_{dc}^{lk} t_{lki}^{dab} t_j^c \\
& + \frac{1}{2} \lambda_{cd}^{kl} t_{ki}^{ca} t_{lj}^{db} \\
& - \frac{1}{4} \lambda_{cd}^{kl} t_{ij}^{ca} t_{kl}^{db} \\
& + \frac{1}{16} \lambda_{cd}^{kl} t_{kl}^{ab} t_{ij}^{cd} \\
& - \frac{1}{4} \lambda_{cd}^{kl} t_{ki}^{ab} t_{lj}^{cd} \\
& - \frac{1}{2} \lambda_{cd}^{kl} t_{ki}^{cd} t_l^a t_j^b \\
& + \frac{1}{8} \lambda_{cd}^{lk} t_{ij}^{cd} t_l^a t_k^b \\
& - \frac{1}{2} \lambda_{cd}^{kl} t_{kl}^{ca} t_i^d t_j^b \\
& - \lambda_{cd}^{kl} t_{ki}^{ca} t_j^d t_l^b \\
& + \frac{1}{8} \lambda_{dc}^{kl} t_{kl}^{ab} t_i^d t_j^c \\
& + \frac{1}{4} \lambda_{dc}^{kl} t_i^d t_j^c t_k^a t_l^b
\end{aligned}$$

Table 6--continued

$$\begin{aligned}
& - \frac{1}{24} \lambda_{cde}^{klm} t_{kli}^{cde} t_{mj}^{ab} \\
& + \frac{1}{48} \lambda_{cde}^{klm} t_{kij}^{cde} t_{lm}^{ab} \\
& - \frac{1}{24} \lambda_{cde}^{klm} t_{cda}^{klm} t_{ij}^{eb} \\
& + \frac{1}{4} \lambda_{cde}^{klm} t_{kli}^{cda} t_{mj}^{eb} \\
& - \frac{1}{8} \lambda_{cde}^{klm} t_{kij}^{cda} t_{lm}^{eb} \\
& + \frac{1}{48} \lambda_{cde}^{klm} t_{klm}^{cab} t_{ij}^{de} \\
& - \frac{1}{8} \lambda_{cde}^{klm} t_{kli}^{cab} t_{mj}^{de} \\
& - \frac{1}{12} \lambda_{cde}^{klm} t_{kli}^{cde} t_m^a t_j^b \\
& + \frac{1}{24} \lambda_{cde}^{kml} t_{kij}^{cde} t_m^a t_l^b \\
& - \frac{1}{12} \lambda_{cde}^{klm} t_{klm}^{cda} t_i^e t_j^b \\
& - \frac{1}{4} \lambda_{cde}^{klm} t_{kli}^{cda} t_j^e t_m^b \\
& + \frac{1}{24} \lambda_{ced}^{klm} t_{klm}^{cab} t_i^e t_j^d \\
& + \frac{1}{4} \lambda_{dec}^{lmk} t_{li}^{de} t_{mk}^{ca} t_j^b \\
& - \frac{1}{2} \lambda_{dec}^{lkm} t_{li}^{de} t_{kj}^{ca} t_m^b \\
& + \frac{1}{8} \lambda_{dec}^{lmk} t_{li}^{de} t_{mk}^{ab} t_j^c \\
& + \frac{1}{8} \lambda_{dec}^{mkl} t_{ij}^{de} t_{mk}^{ca} t_l^b \\
& - \frac{1}{2} \lambda_{dce}^{lmk} t_{lm}^{da} t_{ki}^{cb} t_j^e \\
& + \frac{1}{4} \lambda_{dec}^{lkm} t_{li}^{de} t_j^c t_k^a t_m^b \\
& + \frac{1}{4} \lambda_{dce}^{lmk} t_{lm}^{da} t_i^c t_j^e t_k^b
\end{aligned}$$

Table 6--continued

$$\begin{aligned}
 \Gamma(ab, cd) = & \frac{1}{8} \lambda_{ab}^{ij} t_{ij}^{cd} \\
 & + \frac{1}{4} \lambda_{ab}^{ji} t_j^c t_i^d \\
 & + \frac{1}{24} \lambda_{abe}^{ijk} t_{ijk}^{ecd} \\
 & + \frac{1}{4} \lambda_{abe}^{jki} t_{jk}^{ec} t_i^d
 \end{aligned}$$

$$\begin{aligned}
 \Gamma(kl, ij) = & \frac{1}{8} \lambda_{ab}^{ij} t_{kl}^{ab} \\
 & + \frac{1}{4} \lambda_{ba}^{ij} t_k^b t_l^a \\
 & + \frac{1}{24} \lambda_{abc}^{ijm} t_{mkl}^{abc} \\
 & + \frac{1}{4} \lambda_{bca}^{ijm} t_{mk}^{bc} t_l^a
 \end{aligned}$$

$$\begin{aligned}
 \Gamma(ja, bi) = & \lambda_a^i t_j^b \\
 & + \lambda_{ac}^{ik} t_{kj}^{cb} \\
 & - \lambda_{ac}^{ik} t_j^c t_k^b \\
 & + \frac{1}{4} \lambda_{adc}^{ilk} t_{lkj}^{dcb} \\
 & - \frac{1}{2} \lambda_{adc}^{ikl} t_{kj}^{dc} t_l^b \\
 & - \frac{1}{2} \lambda_{acd}^{ilk} t_{lk}^{cb} t_j^d
 \end{aligned}$$

$$\begin{aligned}
 \Gamma(ai, bc) = & \frac{1}{2} \lambda_a^j t_{ji}^{bc} \\
 & + \lambda_a^j t_j^b t_i^c \\
 & - \frac{1}{4} \lambda_{ad}^{kj} t_{kji}^{dbc} \\
 & - \frac{1}{2} \lambda_{ad}^{jk} t_{jk}^{db} t_i^c \\
 & + \lambda_{ad}^{jk} t_{ji}^{db} t_k^c \\
 & - \frac{1}{4} \lambda_{ad}^{jk} t_{jk}^{bc} t_i^d
 \end{aligned}$$

Table 6--continued

$$\begin{aligned}
& - \frac{1}{2} \lambda_{ad}^{kj} t_k^b t_i^d t_j^c \\
& + \frac{1}{12} \lambda_{ade}^{jkl} t_{jkl}^{deb} t_i^c \\
& - \frac{1}{4} \lambda_{ade}^{jkl} t_{jki}^{deb} t_l^c \\
& + \frac{1}{12} \lambda_{ade}^{jkl} t_{jkl}^{dbc} t_i^e \\
& + \frac{1}{8} \lambda_{aed}^{klj} t_{ki}^{ed} t_{lj}^{bc} \\
& - \frac{1}{2} \lambda_{ade}^{klj} t_{kl}^{db} t_{ji}^{ec} \\
& + \frac{1}{4} \lambda_{aed}^{kjl} t_{ki}^{ed} t_j^b t_l^c \\
& + \frac{1}{2} \lambda_{aed}^{klj} t_{kl}^{eb} t_i^d t_j^c \\
& - \frac{1}{2} \lambda_{bc}^{ij} t_j^a \\
& + \frac{1}{4} \lambda_{bcd}^{ikj} t_{kj}^{da} \\
\\
\Gamma(jk, ia) = & - \frac{1}{2} \lambda_b^i t_{jk}^{ba} \\
& - \lambda_b^i t_j^b t_k^a \\
& + \frac{1}{4} \lambda_{cb}^{il} t_{ljk}^{cba} \\
& + \frac{1}{2} \lambda_{bc}^{il} t_{lj}^{bc} t_k^a \\
& + \frac{1}{4} \lambda_{bc}^{il} t_{jk}^{bc} t_l^a \\
& - \lambda_{bc}^{il} t_{lj}^{ba} t_k^c \\
& + \frac{1}{2} \lambda_{cb}^{il} t_j^c t_k^b t_l^a \\
& - \frac{1}{12} \lambda_{bcd}^{ilm} t_{lmj}^{bcd} t_k^a \\
& - \frac{1}{12} \lambda_{bcd}^{ilm} t_{ljk}^{bcd} t_m^a \\
& + \frac{1}{4} \lambda_{bcd}^{ilm} t_{lmj}^{bca} t_k^d \\
& - \frac{1}{8} \lambda_{cdb}^{iml} t_{jk}^{cd} t_{ml}^{ba}
\end{aligned}$$

Table 6--continued

$$\begin{aligned}
& + \frac{1}{2} \lambda_{cdb}^{ilm} t_{lj}^{ca} t_{mk}^{db} \\
& - \frac{1}{2} \lambda_{cdb}^{ilm} t_{lj}^{cd} t_k^b t_m^a \\
& - \frac{1}{4} \lambda_{cbd}^{iml} t_{ml}^{ca} t_j^b t_k^d \\
& + \frac{1}{2} \lambda_{ab}^{jk} t_i^b \\
& - \frac{1}{4} \lambda_{acb}^{jkl} t_{li}^{cb}
\end{aligned}$$

Note: Summation over all but the target labels is implied.

Table 7. The A0 Derivative Part of the Coupled-Cluster and MBPT Energy Derivatives.

$$\text{A0 derivative part} = \sum_{\substack{\mu, \nu, \\ \rho, \sigma}} \langle \mu(\chi) \nu(\chi) | \rho(\chi) \sigma(\chi) \rangle^{\chi} \Gamma(\mu \nu \rho \sigma) ,$$

where

$$\begin{aligned} \Gamma(\mu \nu \rho \sigma) = & \sum_{\substack{i, j \\ a, b}} \Gamma(ij, ab) (C_{\rho a} C_{\sigma b} - C_{\rho b} C_{\sigma a}) C_{\mu i}^* C_{\nu j}^* \\ & + \sum_{\substack{a, b \\ c, d}} \Gamma(ab, cd) (C_{\rho c} C_{\sigma d} - C_{\rho d} C_{\sigma c}) C_{\mu a}^* C_{\nu b}^* \\ & + \sum_{\substack{i, j \\ k, l}} \Gamma(ij, kl) (C_{\rho k} C_{\sigma l} - C_{\rho l} C_{\sigma k}) C_{\mu i}^* C_{\nu j}^* \\ & + \sum_{\substack{i, a \\ j, b}} \Gamma(ja, bi) (C_{\rho b} C_{\sigma i} - C_{\rho i} C_{\sigma b}) C_{\mu j}^* C_{\nu a}^* \\ & + \sum_{\substack{i, a \\ b, c}} \Gamma(ai, bc) (C_{\rho b} C_{\sigma c} - C_{\rho c} C_{\sigma b}) C_{\mu a}^* C_{\nu i}^* \\ & + \sum_{\substack{i, a \\ j, k}} \Gamma(jk, ia) (C_{\rho i} C_{\sigma a} - C_{\rho a} C_{\sigma i}) C_{\mu j}^* C_{\nu k}^* \end{aligned}$$

Note: $\langle \mu \nu | \rho \sigma \rangle^{\chi}$ denotes the derivative of an ordinary A0 two-electron integral, evaluated at $\chi=0$.

Table 8. The I and X Intermediates Used in the Evaluation of CCSDT and MBPT Energy Derivatives.

$$\begin{aligned}
 I_{ij} = & -1/2 (\Gamma(jk,ab) - \Gamma(kj,ab)) \langle ik||ab \rangle \\
 & -1/2 (\Gamma(jl,mk) - \Gamma(lj,mk) + \Gamma(mk,jl) - \Gamma(mk,lj)) \langle il||mk \rangle \\
 & -1/2 (\Gamma(ja,bk) + \Gamma(kb,aj)) \langle ia||bk \rangle \\
 & -1/2 \Gamma(aj,bc) \langle ai||bc \rangle \\
 & -1/2 (\Gamma(jk,la) - \Gamma(kj,la)) \langle ik||la \rangle \\
 & -1/2 \Gamma(lk,ja) \langle lk||ia \rangle
 \end{aligned}$$

$$\begin{aligned}
 I_{ab} = & -1/2 (\Gamma(ij,bc) - \Gamma(ij,cb)) \langle ij||ac \rangle \\
 & -1/2 (\Gamma(be,cd) - \Gamma(eb,cd) + \Gamma(cd,be) - \Gamma(cd,eb)) \langle ae||cd \rangle \\
 & -1/2 (\Gamma(jb,ci) + \Gamma(ic,bj)) \langle ja||ci \rangle \\
 & -1/2 \Gamma(bi,cd) \langle ai||cd \rangle \\
 & -1/2 (\Gamma(di,bc) - \Gamma(di,cb)) \langle di||ac \rangle \\
 & -1/2 \Gamma(jk,ib) \langle jk||ia \rangle
 \end{aligned}$$

$$\begin{aligned}
 I_{ai} = & -1/2 (\Gamma(kj,ab) - \Gamma(kj,ba)) \langle kj||ib \rangle \\
 & -1/2 (\Gamma(ab,cd) - \Gamma(ba,cd) + \Gamma(cd,ab) - \Gamma(cd,ba)) \langle ib||cd \rangle \\
 & -1/2 (\Gamma(ja,bk) + \Gamma(kb,aj)) \langle ji||bk \rangle \\
 & -1/2 \Gamma(aj,bc) \langle ij||bc \rangle \\
 & -1/2 (\Gamma(dj,ac) - \Gamma(dj,ca)) \langle dj||ic \rangle \\
 & -1/2 \Gamma(jk,la) \langle jk||li \rangle
 \end{aligned}$$

Table 8--continued

$$\begin{aligned}
X_{ai} = & I_{ai} \\
& +1/2 D_{kj} (\langle ka||ji\rangle + \langle ki||ja\rangle) \\
& +1/2 D_{cb} (\langle ca||bi\rangle + \langle ci||ba\rangle) \\
& +1/2 (\Gamma(ij,cb) - \Gamma(ji,cb)) \langle aj||cb\rangle \\
& +1/2 (\Gamma(il,kj) - \Gamma(li,kj) + \Gamma(kj,il) - \Gamma(kj,li)) \langle al||kj\rangle \\
& +1/2 (\Gamma(ic,bj) + \Gamma(jb,ci)) \langle ac||bj\rangle \\
& +1/2 \Gamma(di,bc) \langle da||bc\rangle \\
& +1/2 (\Gamma(ik,jb) - \Gamma(ki,jb)) \langle ak||jb\rangle \\
& +1/2 \Gamma(jk,ib) \langle jk||ab\rangle
\end{aligned}$$

Note: Summation over all but the target labels is implied.

The occupied-occupied and virtual-virtual blocks of the CCSDT density matrix D are given in Table (5).

The Γ intermediates are defined in Table (6).

MBPT Energy Derivatives

Now we extract the finite-order MBPT derivative from the CCSDT derivative energy expression. Inspection of Equation (34) reveals that for the derivative of the n^{th} -order correlation energy, the n^{th} -order MBPT density matrix D and the n^{th} -order I intermediates are required. We specify the construction of the occupied-occupied and virtual-virtual blocks of the density matrix D and the Γ intermediates appropriate for various MBPT models in Tables (9) through (12). The X and I intermediates are to be subsequently constructed as given in Table (8), using the Γ 's and the two blocks of D so defined. The appropriate n^{th} -order virtual-occupied block of D is obtained by solving Equation (33) using the resultant X intermediate. Finally, the appropriate n^{th} -order AO derivative part is obtained by using the same set of Γ intermediates.

The expressions in the MBPT tables (Tables (9-12)) are in terms of the low-order iterates of T and the function $Q_{ij}^{ab}(A, B \times C)$. We summarize the low-order iterates of Λ and T and define related quantities in Table (13).

Summary of Computational Strategy

The overall strategy for computing MBPT/CC gradients is:

- 1) Obtain S^X and Q^X for all $3N$ degrees of freedom. (See Equations (25) and (26).)
- 2a) If an n^{th} -order MBPT gradient is desired, solve the unperturbed MBPT problem by low-order iteration of the CC t -amplitude

Table 9. Summary for the MBPT(2) Model.

$$D_{ij} = \frac{1}{2} t_{jk}^{ab(1)} t_{ki}^{ab(1)}$$

$$D_{ab} = -\frac{1}{2} t_{ij}^{ac(1)} t_{ij}^{cb(1)}$$

$$\Gamma(ij,ab) = \frac{1}{2} t_{ij}^{ab(1)} ; \quad \text{all other } \Gamma\text{'s} = 0$$

Note: Summation over all but target labels is implied.

Table 10. Summary for the MBPT(3) Model.

$$D_{ij} = \frac{1}{2} t_{jk}^{ab(1)} t_{ki}^{ab(2)} + \frac{1}{2} \Delta t_{jk}^{ab(2)} t_{ki}^{ab(1)}$$

$$D_{ab} = -\frac{1}{2} t_{ij}^{ac(1)} t_{ij}^{cb(2)} - \frac{1}{2} \Delta t_{ij}^{ac(2)} t_{ij}^{cb(1)}$$

$$\Gamma(ij,ab) = \frac{1}{2} t_{ij}^{ab(2)}$$

$$\Gamma(ab,cd) = \frac{1}{8} t_{ij}^{ab(1)} t_{ij}^{cd(1)}$$

$$\Gamma(kl,ij) = \frac{1}{8} t_{ij}^{ab(1)} t_{kl}^{ab(1)}$$

$$\Gamma(ja,bi) = t_{ik}^{ac(1)} t_{kj}^{cb(1)} ; \quad \Gamma(ai,bc) = \Gamma(jk,ia) = 0$$

Note: Summation over all but target labels is implied.

Table 11. Summary for the MBPT(4) Model.

$$\begin{aligned}
D_{ij} = & - t_j^a(2) t_i^a(2) \\
& + \frac{1}{2} t_{jk}^{ab}(1) t_{ki}^{ab}(3) + \frac{1}{2} \Delta t_{jk}^{ab}(2) t_{ki}^{ab}(2) + \frac{1}{2} \Delta \lambda_{ab}^{jk}(3) t_{ki}^{ab}(1) \\
& - \frac{1}{12} t_{jlk}^{abc}(2) t_{lki}^{abc}(2)
\end{aligned}$$

$$\begin{aligned}
D_{ab} = & t_i^a(2) t_i^b(2) \\
& - \frac{1}{2} t_{ij}^{ac}(1) t_{ij}^{cb}(3) - \frac{1}{2} \Delta t_{ij}^{ac}(2) t_{ij}^{cb}(2) - \frac{1}{2} \Delta \lambda_{ac}^{ij}(3) t_{ij}^{cb}(1) \\
& + \frac{1}{12} t_{ijk}^{adc}(2) t_{ijk}^{dcb}(2)
\end{aligned}$$

$$\begin{aligned}
\Gamma(ij, ab) = & \frac{1}{2} t_{ij}^{ab}(3) + \frac{1}{4} Q_{ij}^{ab}(t(1), t(1) \times I) / D_{ij}^{ab} \\
& + \frac{1}{4} Q_{ij}^{ab}(t(1), I \times t(1)) / D_{ij}^{ab} + \frac{1}{4} Q_{ij}^{ab}(I, t(1) \times t(1)) / D_{ij}^{ab} \\
& + \frac{1}{4} Q_{ij}^{ab}(t(1), t(1) \times t(1))
\end{aligned}$$

$$\Gamma(ab, cd) = \frac{1}{8} t_{ij}^{ab}(1) t_{ij}^{cd}(2) + \frac{1}{8} \Delta t_{ij}^{ab}(2) t_{ij}^{cd}(1)$$

$$\Gamma(kl, ij) = \frac{1}{8} t_{ij}^{ab}(1) t_{kl}^{ab}(2) + \frac{1}{8} \Delta t_{ij}^{ab}(2) t_{kl}^{ab}(1)$$

$$\Gamma(ja, bi) = t_{ik}^{ac}(1) t_{kj}^{cb}(2) + \Delta t_{ik}^{ac}(2) t_{kj}^{cb}(1)$$

$$\Gamma(ai, bc) = t_j^a(2) t_{ji}^{bc}(1) + \frac{1}{2} t_{ikj}^{bcd}(2) t_{kj}^{da}(1)$$

$$\Gamma(jk, ia) = - t_i^b(2) t_{jk}^{ba}(1) - \frac{1}{2} t_{jkl}^{acb}(2) t_{li}^{cb}(1)$$

Note: Summation over all but target labels is implied.

Table 12. Summary for the LCCD (or D-MBPT(∞)) Model.

$$D_{ij} = \frac{1}{2} t_{jk}^{ab(\infty)} t_{ki}^{ab(\infty)}$$

$$D_{ab} = -\frac{1}{2} t_{ij}^{ac(\infty)} t_{ij}^{cb(\infty)}$$

$$\Gamma(ij, ab) = \frac{1}{2} t_{ij}^{ab(\infty)}$$

$$\Gamma(ab, cd) = \frac{1}{8} t_{ij}^{ab(\infty)} t_{ij}^{cd(\infty)}$$

$$\Gamma(kl, ij) = \frac{1}{8} t_{ij}^{ab(\infty)} t_{kl}^{ab(\infty)}$$

$$\Gamma(ja, bi) = t_{ik}^{ac(\infty)} t_{kj}^{cb(\infty)} \quad ; \quad \Gamma(ai, bc) = \Gamma(jk, ia) = 0$$

Note: Summation over all but target labels is implied.

The symbol $t_{ij}^{ab(\infty)}$ represents the converged LCCD amplitudes.

Table 13. The Low-order Iterates of Λ and T .

$$t_{ij}^{ab}(1) = \lambda_{ab}^{ij}(1) = \langle ij || ab \rangle / D_{ij}^{ab}$$

$$D_{ij}^{ab} = \epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b$$

$$t_{ij}^{ab}(2) = \lambda_{ab}^{ij}(2) = t_{ij}^{ab}(1) + \Delta t_{ij}^{ab}(2)$$

$$\Delta t_{ij}^{ab}(2) = \left[\frac{1}{2} t_{ij}^{cd}(1) \langle ab || cd \rangle + \frac{1}{2} t_{kl}^{ab}(1) \langle ij || kl \rangle + P(ab|ij) t_{ki}^{ca}(1) \langle jc || bk \rangle \right] / D_{ij}^{ab}$$

$$t_{ij}^{ab}(3) = t_{ij}^{ab}(1) + \Delta t_{ij}^{ab}(2) + \Delta t_{ij}^{ab}(3; \text{SDT}) + \Delta t_{ij}^{ab}(3; 0)$$

$$\lambda_{ab}^{ij}(3) = t_{ij}^{ab}(1) + \Delta t_{ij}^{ab}(2) + \Delta t_{ij}^{ab}(3; \text{SDT}) + \Delta \lambda_{ab}^{ij}(3; 0)$$

$$\Delta t_{ij}^{ab}(3; 0) = Q_{ij}^{ab}(I, t(1) \times t(1)) / D_{ij}^{ab}$$

$$\Delta \lambda_{ab}^{ij}(3; 0) = \{Q_{ij}^{ab}(t(1), I \times t(1)) + Q_{ij}^{ab}(t(1), t(1) \times I)\} / D_{ij}^{ab}$$

$$t(1) = t_{ij}^{ab}(1) \quad I = \langle ij || ab \rangle$$

$$Q_{ij}^{ab}(A, B \times C) = \frac{1}{4} A_{kl}^{cd} \left[B_{ij}^{cd} C_{kl}^{ab} - 2 \left(B_{ij}^{ac} C_{kl}^{bd} + B_{ij}^{bd} C_{kl}^{ac} \right) - 2 \left(B_{ik}^{ab} C_{jl}^{cd} + B_{jl}^{ab} C_{ik}^{cd} \right) + 4 \left(B_{ki}^{ac} C_{lj}^{bd} + B_{ki}^{bd} C_{lj}^{ac} \right) \right]$$

$$\begin{aligned} \Delta t_{ij}^{ab}(3; \text{SDT}) = & \left[\frac{1}{2} \Delta t_{ij}^{cd}(2) \langle ab || cd \rangle + \frac{1}{2} \Delta t_{kl}^{ab}(2) \langle ij || kl \rangle \right. \\ & + P(ab|ij) \Delta t_{ki}^{ca}(2) \langle jc || bk \rangle \\ & + P(ij) t_i^c(2) \langle cj || ab \rangle - P(ab) t_k^a(2) \langle ij || kb \rangle \\ & \left. + \frac{1}{2} P(ab) t_{kij}^{cda}(2) \langle cd || bk \rangle - \frac{1}{2} P(ab) t_{kli}^{cab}(2) \langle jc || kl \rangle \right] / D_{ij}^{ab} \end{aligned}$$

Table 13--continued

$$t_i^a(2) = \lambda_a^i(2) = \left[-\frac{1}{2} t_{ji}^{bc}(1) \langle bc || aj \rangle + \frac{1}{2} t_{jk}^{ba}(1) \langle ib || jk \rangle \right] / D_i^a$$

$$D_i^a = \epsilon_i - \epsilon_a$$

$$t_{ijk}^{abc}(2) = \lambda_{abc}^{ijk}(2) = \left[-P(a/bc|k/ij) t_{ij}^{da}(1) \langle dk || bc \rangle \right. \\ \left. + P(c/ab|i/jk) t_{ii}^{ab}(1) \langle jk || lc \rangle \right] / D_{ijk}^{abc}$$

$$D_{ijk}^{abc} = \epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c$$

Note: Summation over all but target labels is implied.

equations. Save the t -amplitude iterates through $n-1^{\text{th}}$ order in the correlation perturbation.

- b) Or if a CC gradient is desired, solve the unperturbed CC problem by converging the CC t -amplitude equations. Save the converged t -amplitudes.
- 3a) If an MBPT gradient is desired, construct the Γ intermediates and the occupied-occupied and virtual-virtual blocks of the density matrix D from the low-order iterates of the CC t -amplitude equations. (See Tables (9-12).)
- 3b) Or if a CC gradient is desired, it is necessary to solve the linear equation for the λ -amplitudes using the converged t -amplitudes. Then construct the Γ intermediates as given in Table (6) and construct the occupied-occupied and virtual-virtual blocks of the density matrix D as given in Table (5).
- 4) Transform the Γ intermediates to the A0 basis; compute the A0 derivative contributions for each of the $3N$ degrees of freedom. (See Table (7).)
- 5) Using the Γ intermediates and the occupied-occupied and virtual-virtual blocks of the relaxed density matrix D , construct the intermediates I and X as given in Table (8).
- 6) Solve Equation (33) to obtain the virtual-occupied block of the density matrix.
- 7) Evaluate the simple dot-products in Equation (34) for each of the $3N$ degrees of freedom; add to the corresponding A0 derivative contributions to obtain the total derivative of the correlation energy for each degree of freedom.

(Note: In Equation (34) the density D , the perturbation matrix Q^X and overlap derivative matrix S^X are in terms of the MO basis. The

3N sets of S^X and Q^X matrices are initially prepared in the AO basis before an MO transformation. (See Equations (25) and (26).) It is more efficient to avoid 3N sets of transformations by instead transforming the perturbation-independent matrices D and I to the AO basis. The contributions of Equation (34) can then be computed equivalently as dot products of matrices in the AO basis.)

- 8) Option: Since the MBPT/CC relaxed density is available, one may readily compute one-electron response properties or plot the electronic density of the molecular system.

SECOND DERIVATIVES OF THE COUPLED-CLUSTER ENERGY

Derivation of General Expressions

Let us again return to Equation (6), where the Hamiltonian is in normal-ordered form and the wavefunction is the exponential of the Coupled-Cluster model. Let there be two perturbation parameters α and β , upon which the Hamiltonian, the wavefunction, and ΔE are dependent.

$$e^{-T(\alpha, \beta)} H_N(\alpha, \beta) e^{T(\alpha, \beta)} |0\rangle = \Delta E(\alpha, \beta) |0\rangle \quad (35)$$

Let us define the following:

$$T = T(\alpha, \beta) \Big|_{\alpha=\beta=0} \quad T^\alpha = \frac{\partial T(\alpha, \beta)}{\partial \alpha} \Big|_{\alpha=\beta=0} \quad T^\beta = \frac{\partial T(\alpha, \beta)}{\partial \beta} \Big|_{\alpha=\beta=0}$$

$$T^{\alpha\beta} = \frac{\partial^2 T(\alpha, \beta)}{\partial \alpha \partial \beta} \Big|_{\alpha=\beta=0}$$

$$H_N = f_N + W_N = f_N(\alpha, \beta) \Big|_{\alpha=\beta=0} + W_N(\alpha, \beta) \Big|_{\alpha=\beta=0}$$

$$H_N^\alpha = f_N^\alpha + W_N^\alpha = \left(\frac{\partial f_N(\alpha, \beta)}{\partial \alpha} + \frac{\partial W_N(\alpha, \beta)}{\partial \alpha} \right) \Big|_{\alpha=\beta=0}$$

$$H_N^\beta = f_N^\beta + W_N^\beta = \left(\frac{\partial f_N(\alpha, \beta)}{\partial \beta} + \frac{\partial W_N(\alpha, \beta)}{\partial \beta} \right) \Big|_{\alpha=\beta=0}$$

$$H_N^{\alpha\beta} = f_N^{\alpha\beta} + W_N^{\alpha\beta} = \left(\frac{\partial^2 f_N(\alpha, \beta)}{\partial \alpha \partial \beta} + \frac{\partial^2 W_N(\alpha, \beta)}{\partial \alpha \partial \beta} \right) \Big|_{\alpha=\beta=0}$$

$$\Delta E = \Delta E(\alpha, \beta) \Big|_{\alpha=\beta=0} \quad \Delta E^\alpha = \frac{\partial \Delta E(\alpha, \beta)}{\partial \alpha} \Big|_{\alpha=\beta=0} \quad \Delta E^\beta = \frac{\partial \Delta E(\alpha, \beta)}{\partial \beta} \Big|_{\alpha=\beta=0}$$

$$\Delta E^{\alpha\beta} = \frac{\partial^2 \Delta E(\alpha, \beta)}{\partial \alpha \partial \beta} \Big|_{\alpha=\beta=0} .$$

As before, projection on the left of Equation (35) by $\langle P|$ and evaluation at $\alpha=\beta=0$, yields the unperturbed Coupled-Cluster expressions. The derivative of Equation (35) with respect to α (or β), evaluated at $\alpha=\beta=0$, is the equivalent of Equation (14) of the previous section:

$$\left([(H_N e^T)_c, T^\alpha] + (H_N^\alpha e^T)_c \right) |0\rangle = \Delta E^\alpha |0\rangle . \quad (36)$$

Or more simply,

$$\left(((H_N e^T)_c T^\alpha)_c + (H_N^\alpha e^T)_c \right) |0\rangle = \Delta E^\alpha |0\rangle .$$

Projection on the left by $\langle P|$ yields the equivalents of Equations (15) and (16): an expression for ΔE^α and a set of linear equations which determine the derivative t-amplitudes:

$$\langle 0 | ((H_N e^T)_c T^\alpha)_c | 0 \rangle + \langle 0 | (H_N^\alpha e^T)_c | 0 \rangle = \Delta E^\alpha \quad (37)$$

and

$$\langle \Phi | ((H_N e^T)_c T^\alpha)_c | 0 \rangle + \langle \Phi | (H_N^\alpha e^T)_c | 0 \rangle = 0 . \quad (38)$$

Although the evaluation of first derivatives does not require the derivative t -amplitudes, the evaluation of second-derivatives does. The coupled, linear equations represented by Equation (38) for the CCSDT-1 model are presented in Tables (14-16).

The second derivative of Equation (35) with respect to α and β , evaluated at $\alpha=\beta=0$, is given by:

$$\begin{aligned} & \left[[(H_N^T e^T)_c, T^{\alpha\beta}] + [(H_N^{\beta T} e^T)_c, T^{\alpha}] + [(H_N^{\alpha T} e^T)_c, T^{\beta}] \right. \\ & \left. + (H_N^{\alpha\beta} e^T)_c + [[(H_N^T e^T)_c, T^{\alpha}], T^{\beta}] \right] |0\rangle = \Delta E^{\alpha\beta} |0\rangle . \end{aligned} \quad (39)$$

Thus,

$$\begin{aligned} & \left((H_N^T e^T)_c T^{\alpha\beta} \right)_c + ((H_N^{\beta T} e^T)_c T^{\alpha})_c + ((H_N^{\alpha T} e^T)_c T^{\beta})_c \\ & + (H_N^{\alpha\beta} e^T)_c + (((H_N^T e^T)_c T^{\alpha})_c T^{\beta})_c \Big) |0\rangle = \Delta E^{\alpha\beta} |0\rangle . \end{aligned}$$

Projection on the left by $\langle P|$ will yield: an expression for $\Delta E^{\alpha\beta}$ in terms of T^{α} , T^{β} , the unperturbed T , and $T^{\alpha\beta}$; and a set of coupled linear equations for the $T^{\alpha\beta}$ amplitudes. The dependence of $\Delta E^{\alpha\beta}$ on $T^{\alpha\beta}$ can be eliminated just as the first derivative T is eliminated from the first derivative of the energy. That is, we return to Equation (39) and insert $\hat{1} = |P\rangle\langle P|$ into the terms containing $T^{\alpha\beta}$. Since $\langle 0|T^{\alpha\beta}|P\rangle=0$ and $\langle \Phi|(H_N^T e^T)_c|0\rangle=0$, we obtain upon left-projection by $|P\rangle$:

$$\begin{aligned} \langle 0 | \left((H_N^{\beta e T})_c T^\alpha + ((H_N^{\alpha e T})_c T^\beta) + (H_N^{\alpha \beta e T})_c + (((H_N^e T)_c T^\alpha)_c T^\beta) \right) | 0 \rangle \\ + \langle 0 | (H_N^e T)_c | \Phi \rangle \langle \Phi | T^{\alpha \beta} | 0 \rangle = \Delta E^{\alpha \beta} \end{aligned}$$

and

$$\begin{aligned} \langle \Phi | -T^{\alpha \beta} | 0 \rangle \Delta E + \langle \Phi | (H_N^e T)_c | \Phi \rangle \langle \Phi | T^{\alpha \beta} | 0 \rangle \\ + \langle \Phi | \left(\underset{[A]}{(H_N^{\beta e T})_c T^\alpha} + \underset{[B]}{((H_N^{\alpha e T})_c T^\beta)} \right. \\ \left. + \underset{[C]}{(H_N^{\alpha \beta e T})_c} + \underset{[D]}{(((H_N^e T)_c T^\alpha)_c T^\beta)} \right) | 0 \rangle = 0 . \end{aligned}$$

The second equation is solved for $\langle \Phi | T^{\alpha \beta} | 0 \rangle$:

$$\langle \Phi | T^{\alpha \beta} | 0 \rangle = - \langle \Phi | (H_N^e T)_c - \Delta E | \Phi \rangle^{-1} \langle \Phi | ([A] + [B] + [C] + [D]) | 0 \rangle ,$$

and we substitute for $\langle \Phi | T^{\alpha \beta} | 0 \rangle$ in the $\Delta E^{\alpha \beta}$ expression:

$$\begin{aligned} \langle 0 | \left((H_N^{\beta e T})_c T^\alpha + ((H_N^{\alpha e T})_c T^\beta) + (H_N^{\alpha \beta e T})_c + (((H_N^e T)_c T^\alpha)_c T^\beta) \right) | 0 \rangle \\ - \langle 0 | ((H_N^e T)_c | \Phi \rangle \langle \Phi | (H_N^e T)_c - \Delta E | \Phi \rangle^{-1} \langle \Phi | ([A] + [B] + [C] + [D]) | 0 \rangle = \Delta E^{\alpha \beta} . \end{aligned}$$

Recalling the definition of the perturbation-independent de-excitation operator Λ , we have

$$\begin{aligned}
& \langle 0 | \left[((H_N^{\beta e T})_c T^\alpha)_c + ((H_N^{\alpha e T})_c T^\beta)_c + (H_N^{\alpha\beta e T})_c + (((H_N e^T)_c T^\alpha)_c T^\beta)_c \right] | 0 \rangle \\
& + \langle 0 | \Lambda | \Phi \rangle \langle \Phi | ([A] + [B] + [C] + [D]) | 0 \rangle = \Delta E^{\alpha\beta} .
\end{aligned}$$

An equivalent form of the above expression can be readily subjected to the usual diagrammatic rules. Recalling that $\hat{i} = |P\rangle\langle P| = |0\rangle\langle 0| + |\Phi\rangle\langle\Phi|$, the second derivative of the energy can be written as

$$\begin{aligned}
\Delta E^{\alpha\beta} = & \langle 0 | ((H_N^{\alpha e T})_c T^\beta)_c | 0 \rangle + \langle 0 | ((H_N^{\beta e T})_c T^\alpha)_c | 0 \rangle \quad (40) \\
& + \langle 0 | (H_N^{\alpha\beta e T})_c | 0 \rangle + \langle 0 | (((H_N e^T)_c T^\alpha)_c T^\beta)_c | 0 \rangle \\
& + \langle 0 | \Lambda ((H_N^{\alpha e T})_c T^\beta)_c | 0 \rangle + \langle 0 | \Lambda ((H_N^{\beta e T})_c T^\alpha)_c | 0 \rangle \\
& + \langle 0 | \Lambda (H_N^{\alpha\beta e T})_c | 0 \rangle + \langle 0 | \Lambda (((H_N e^T)_c T^\alpha)_c T^\beta)_c | 0 \rangle .
\end{aligned}$$

Equation (40) is the general expression for the second derivative of the CC energy. It applies to CC models of any truncation of T or choice of spin-orbital basis. We wish to develop the general second derivative energy expression for the specific choice of the CCSDT-1 model. The first, second, and fourth terms of Equation (40) are easily evaluated, as they reduce to forms analogous to the ordinary CC energy expression:

$$\begin{aligned}
& \frac{1}{4} \langle ab || ij \rangle^\alpha \tau_{ij}^{ab} + \langle ab || ij \rangle^\alpha t_i^a \tau_j^b + f_{ia}^\alpha \tau_i^a \\
& + \frac{1}{4} \langle ab || ij \rangle^\beta \tau_{ij}^{ab} + \langle ab || ij \rangle^\beta t_i^a \tau_j^b + f_{ia}^\beta \tau_i^a \\
& + \langle ab || ij \rangle \tau_i^a \tau_j^b
\end{aligned}$$

where the symbol τ represents the derivative of a t -amplitude with respect to α , evaluated at $\alpha=\beta=0$ and ϵ represents the derivative of a t -amplitude with respect to β , evaluated at $\alpha=\beta=0$.

The third and seventh terms of Equation (40) are exactly the expressions in Table (1), except that the symbol χ is to be interpreted as the derivative with respect to α and β , evaluated at $\alpha=\beta=0$. Of course, Table (1) is for the CCSDT model, but we may simply ignore terms in Table (1) that do not apply to the truncated CCSDT-1 model. The algebraic expressions for the sixth term in the CCSDT-1 model are given in Table (17). The fifth term is obtained from the sixth term by exchanging α and β . Finally, the eighth term is given in Table (18).

Expressions for the Choice of SCF Reference

As in the section on first derivatives of SCF orbitals, all orbitals are assumed to be unperturbed, i.e. evaluated at $\alpha=\beta=0$, unless otherwise shown as a function of α and β . Derivative orbitals, evaluated at $\chi=0$, are indicated by the superscript $\alpha\beta$.

$$\begin{aligned}
|p(\alpha, \beta)\rangle &= \phi_p(\alpha, \beta) & |p\rangle &= |p(\alpha, \beta)\rangle|_{\alpha=\beta=0} & |p^{\alpha\beta}\rangle &= \left. \frac{\partial^2 |p(\alpha, \beta)\rangle}{\partial\alpha\partial\beta} \right|_{\alpha=\beta=0} \\
|\mu(\alpha, \beta)\rangle &= \psi_\mu(\alpha, \beta) & |\mu\rangle &= |\mu(\alpha, \beta)\rangle|_{\alpha=\beta=0} & |\mu^{\alpha\beta}\rangle &= \left. \frac{\partial^2 |\mu(\alpha, \beta)\rangle}{\partial\alpha\partial\beta} \right|_{\alpha=\beta=0}
\end{aligned}$$

The results of CPHF theory for the second derivative of non-canonical

Table 14. The T_1^α Equation for the CCSDT-1 Model.

$$\begin{aligned}
0 = & f_{ia}^\alpha + f_{ba}^\alpha t_i^b - f_{ji}^\alpha t_j^a + \langle aj||ib \rangle^\alpha t_j^b \\
& + f_{jb}^\alpha (t_{ji}^{ba} - t_i^b t_j^a) \\
& + \frac{1}{2} \langle ja||bc \rangle^\alpha c_{ji}^{bc} - \frac{1}{2} \langle jk||bi \rangle^\alpha c_{jk}^{ba} - \frac{1}{2} \langle jk||bc \rangle^\alpha t_i^b t_{jk}^{ac} \\
& - \frac{1}{2} \langle jk||bc \rangle^\alpha t_k^a t_{ji}^{bc} - \langle jk||cb \rangle^\alpha t_k^c (t_{ij}^{ab} - t_j^a t_i^b) \\
& + \frac{1}{4} \langle bc||jk \rangle^\alpha t_{jki}^{bca} \\
& + f_{ba}^\alpha t_i^b - f_{ji}^\alpha t_j^a + \langle aj||ib \rangle^\alpha t_j^b \\
& + f_{jb}^\alpha (t_{ji}^{ba} - t_i^b t_j^a - t_i^b t_j^a) \\
& + \frac{1}{2} \langle ja||bc \rangle^\alpha (\tau_{ji}^{bc} + \tau_j^b t_i^c + t_j^b \tau_i^c - \tau_j^c t_i^b - t_j^c \tau_i^b) \\
& - \frac{1}{2} \langle jk||bi \rangle^\alpha (\tau_{jk}^{ba} + \tau_j^b t_k^a + t_j^b \tau_k^a - \tau_j^b t_k^a - t_j^b \tau_k^a) \\
& - \frac{1}{2} \langle jk||bc \rangle^\alpha (\tau_i^b t_{jk}^{ac} + t_i^b \tau_{jk}^{ac}) \\
& - \frac{1}{2} \langle jk||bc \rangle^\alpha (\tau_k^a t_{ji}^{bc} + t_k^a \tau_{ji}^{bc}) \\
& - \langle jk||cb \rangle^\alpha \{ \tau_k^c (t_{ij}^{ab} - t_j^a t_i^b) + t_k^c (\tau_{ij}^{ab} - \tau_j^a t_i^b - t_j^a \tau_i^b) \} \\
& + \frac{1}{4} \langle bc||jk \rangle^\alpha \tau_{jki}^{bca}
\end{aligned}$$

where we define

$$c_{ij}^{ab} = t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a$$

Note: Summation over all but target labels is implied.

Table 15. The T_2^α Equation for the CCSDT-1 Model.

$$\begin{aligned}
0 = & \langle ij || ab \rangle^\alpha + (f_{bd}^\alpha + \langle bk || dc \rangle^\alpha t_k^c) t_{ij}^{ad} \\
& + (f_{bd}^\alpha + \langle ak || dc \rangle^\alpha t_k^c) t_{ij}^{db} \\
& - (f_{bd}^\alpha + \langle lk || cj \rangle^\alpha t_l^c) t_{ik}^{ab} \\
& - (f_{bd}^\alpha + \langle lk || ci \rangle^\alpha t_l^c) t_{kj}^{ab} \\
& - (t_k^a t_{ij}^{db} + t_k^b t_{ij}^{ad} + t_i^d t_{kj}^{ab} + t_j^d t_{ik}^{ab}) f_{kd}^\alpha \\
& - \langle ab || cd \rangle^\alpha C_{ij}^{cd} + \langle ij || kl \rangle^\alpha C_{kl}^{ab} \\
& + t_i^c \langle kl || cj \rangle^\alpha C_{kl}^{ab} + t_j^c \langle kl || ic \rangle^\alpha C_{kl}^{ab} \\
& - \langle bk || jd \rangle^\alpha \tilde{C}_{ki}^{ad} + \langle bk || id \rangle^\alpha \tilde{C}_{kj}^{ad} + \langle ak || jd \rangle^\alpha \tilde{C}_{kj}^{ad} - \langle ak || id \rangle^\alpha \tilde{C}_{jk}^{db} \\
& - t_j^c \langle bk || cd \rangle^\alpha \tilde{C}_{ki}^{ad} + t_i^c \langle bk || cd \rangle^\alpha \tilde{C}_{kj}^{ad} \\
& - t_j^c \langle ak || cd \rangle^\alpha \tilde{C}_{ik}^{db} + t_i^c \langle ak || cd \rangle^\alpha \tilde{C}_{jk}^{db} \\
& + t_l^a \langle lk || cj \rangle^\alpha t_{ik}^{cb} - t_l^a \langle lk || ci \rangle^\alpha t_{jk}^{cb} + \frac{1}{4} t_l^a \langle bl || cd \rangle^\alpha E_{ij}^{cd} \\
& - t_l^b \langle lk || cj \rangle^\alpha t_{ik}^{ca} + t_l^b \langle lk || ci \rangle^\alpha t_{jk}^{ca} - \frac{1}{4} t_l^b \langle al || cd \rangle^\alpha E_{ij}^{cd} \\
& - t_k^b \langle ak || ij \rangle^\alpha + t_k^a \langle kb || ij \rangle^\alpha + t_i^c \langle ab || cj \rangle^\alpha + t_j^c \langle ab || ic \rangle^\alpha \\
& + \frac{1}{4} \langle kl || cd \rangle^\alpha [C_{ij}^{cd} C_{kl}^{ab} - 2(t_{ij}^{ac} C_{kl}^{bd} + t_{ij}^{bd} C_{kl}^{ac}) \\
& - 2(t_{ik}^{ab} C_{jl}^{cd} + t_{jl}^{ab} C_{ik}^{cd}) + 4(C_{ki}^{ac} C_{lj}^{bd} + C_{ki}^{bd} C_{lj}^{ac}) \\
& - 8 t_i^d t_k^b t_l^a t_j^c] \\
& + f_{ck}^\alpha t_{kij}^{cab} + \frac{1}{2} P(a/b) \langle cd || bk \rangle^\alpha t_{kij}^{cda} - \frac{1}{2} P(i/j) \langle jc || kl \rangle^\alpha t_{kli}^{cab} \\
& + f_{bd} t_{ij}^{ad} + \langle bk || dc \rangle (t_k^c t_{ij}^{ad} + t_k^c t_{ij}^{ad}) \\
& + f_{bd} t_{ij}^{db} + \langle ak || dc \rangle (t_k^c t_{ij}^{db} + t_k^c t_{ij}^{db}) \\
& - f_{bd} t_{ik}^{ab} - \langle lk || cj \rangle (t_l^c t_{ik}^{ab} + t_l^c t_{ik}^{ab}) \\
& - f_{bd} t_{kj}^{ab} + \langle lk || ci \rangle (t_l^c t_{kj}^{ab} + t_l^c t_{kj}^{ab})
\end{aligned}$$

Table 15--continued

$$\begin{aligned}
& - (\tau_k^a t_{ij}^{db} + \tau_k^b t_{ij}^{ad} + \tau_i^d t_{kj}^{ab} + \tau_j^d t_{ik}^{ab}) f_{kd} \\
& - (\tau_k^a t_{ij}^{db} + \tau_k^b t_{ij}^{ad} + \tau_i^d t_{kj}^{ab} + \tau_j^d t_{ik}^{ab}) f_{kd} \\
& - \langle ab || cd \rangle (C_{ij}^{cd})^\alpha + \langle ij || kl \rangle (C_{kl}^{ab})^\alpha \\
& + \tau_i^c \langle kl || cj \rangle C_{kl}^{ab} + \tau_j^c \langle kl || ic \rangle C_{kl}^{ab} \\
& + \tau_i^c \langle kl || cj \rangle (C_{kl}^{ab})^\alpha + \tau_j^c \langle kl || ic \rangle (C_{kl}^{ab})^\alpha \\
& - \langle bk || jd \rangle (\tilde{C}_{kl}^{ad})^\alpha + \langle bk || id \rangle (\tilde{C}_{kj}^{ad})^\alpha + \langle ak || jd \rangle (\tilde{C}_{ik}^{db})^\alpha - \langle ak || id \rangle (\tilde{C}_{jk}^{db})^\alpha \\
& - \tau_j^c \langle bk || cd \rangle \tilde{C}_{ki}^{ad} + \tau_i^c \langle bk || cd \rangle \tilde{C}_{kj}^{ad} \\
& - \tau_j^c \langle ak || cd \rangle \tilde{C}_{ik}^{db} + \tau_i^c \langle ak || cd \rangle \tilde{C}_{jk}^{db} \\
& - \tau_j^c \langle bk || cd \rangle (\tilde{C}_{ki}^{ad})^\alpha + \tau_i^c \langle bk || cd \rangle (\tilde{C}_{kj}^{ad})^\alpha \\
& - \tau_j^c \langle ak || cd \rangle (\tilde{C}_{ik}^{db})^\alpha + \tau_i^c \langle ak || cd \rangle (\tilde{C}_{jk}^{db})^\alpha \\
& + \tau_1^a \langle lk || cj \rangle t_{ik}^{cb} - \tau_1^a \langle lk || ci \rangle t_{jk}^{cb} + \frac{1}{4} \tau_1^a \langle bl || cd \rangle E_{ij}^{cd} \\
& - \tau_1^b \langle lk || cj \rangle t_{ik}^{ca} + \tau_1^b \langle lk || ci \rangle t_{jk}^{ca} - \frac{1}{4} \tau_1^b \langle al || cd \rangle E_{ij}^{cd} \\
& + \tau_1^a \langle lk || cj \rangle t_{ik}^{cb} - \tau_1^a \langle lk || ci \rangle t_{jk}^{cb} + \frac{1}{4} \tau_1^a \langle bl || cd \rangle (E_{ij}^{cd})^\alpha \\
& - \tau_1^b \langle lk || cj \rangle t_{ik}^{ca} + \tau_1^b \langle lk || ci \rangle t_{jk}^{ca} - \frac{1}{4} \tau_1^b \langle al || cd \rangle (E_{ij}^{cd})^\alpha \\
& - \tau_k^b \langle ak || ij \rangle + \tau_k^a \langle kb || ij \rangle + \tau_i^c \langle ab || cj \rangle + \tau_j^c \langle ab || ic \rangle \\
& + \frac{1}{4} \langle kl || cd \rangle [(C_{ij}^{cd})^\alpha C_{kl}^{ab} - 2(\tau_{ij}^{ac} C_{kl}^{bd} + \tau_{ij}^{bd} C_{kl}^{ac}) \\
& \quad + C_{ij}^{cd} (C_{kl}^{ab})^\alpha - 2(\tau_{ij}^{ac} (C_{kl}^{bd})^\alpha + \tau_{ij}^{bd} (C_{kl}^{ac})^\alpha) \\
& \quad - 2(\tau_{ik}^{ab} C_{jl}^{cd} + \tau_{jl}^{ab} C_{ik}^{cd}) + 4((C_{ki}^{ac})^\alpha C_{lj}^{bd} + (C_{ki}^{bd})^\alpha C_{lj}^{ac}) \\
& \quad - 2(\tau_{ik}^{ab} (C_{jl}^{cd})^\alpha + \tau_{jl}^{ab} (C_{ik}^{cd})^\alpha) + 4(C_{ki}^{ac} (C_{lj}^{bd})^\alpha + C_{ki}^{bd} (C_{lj}^{ac})^\alpha) \\
& \quad - 8(\tau_i^d t_k^b t_1^a t_j^c + \tau_i^d t_k^b t_1^a t_j^c + \tau_i^d t_k^b t_1^a t_j^c + \tau_i^d t_k^b t_1^a t_j^c)] \\
& + f_{ck} \tau_{kij}^{cab} + \frac{1}{2} P(a/b) \langle cd || bk \rangle \tau_{kij}^{cda} - \frac{1}{2} P(i/j) \langle jc || kl \rangle \tau_{kli}^{cab}
\end{aligned}$$

Table 15--continued

where we define

$$C_{ij}^{ab} = t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a$$

$$(C_{ij}^{ab})^\alpha = \tau_{ij}^{ab} + \tau_i^a t_j^b - \tau_i^b t_j^a + t_i^a \tau_j^b - t_i^b \tau_j^a$$

$$\tilde{C}_{ij}^{ab} = t_{ij}^{ab} + t_i^a t_j^b \quad (\tilde{C}_{ij}^{ab})^\alpha = \tau_{ij}^{ab} + \tau_i^a t_j^b + t_i^b \tau_j^a$$

$$E_{ij}^{ab} = t_{ij}^{ab} - t_i^a t_j^b + t_i^b t_j^a$$

$$(E_{ij}^{ab})^\alpha = \tau_{ij}^{ab} - \tau_i^a t_j^b + \tau_i^b t_j^a - t_i^a \tau_j^b + t_i^b \tau_j^a$$

Note: Summation over all but target labels is implied.

Table 16. The T_3^α Equation for the CCSDT-1 Model.

$$\begin{aligned}
0 = & - P(k/ij) t_{ij}^{abc} f_{kl}^\alpha - P(k/ij) \tau_{lij}^{abc} f_{kl} \\
& + P(c/ab) t_{ijk}^{dab} f_{dc}^\alpha + P(c/ab) \tau_{ijk}^{dab} f_{dc} \\
& - P(a/bc|k/ij) t_{ij}^{da} \langle dk||bc \rangle^\alpha - P(a/bc|k/ij) \tau_{ij}^{da} \langle dk||bc \rangle \\
& + P(c/ab|i/jk) t_{li}^{ab} \langle jk||lc \rangle^\alpha + P(c/ab|i/jk) \tau_{li}^{ab} \langle jk||lc \rangle
\end{aligned}$$

Note: Summation over all but target labels is implied.

Table 17. Contributions to the Second Derivative of the CCSDT-1 Energy from:

$$\langle 0 | \Lambda ((H_{Ne}^{\beta T})_c T^{\alpha})_c | 0 \rangle.$$

$$\begin{aligned} \tau_i^a \times [& \lambda_b^i f_{ba}^{\beta} \\ & - \lambda_a^j f_{ij}^{\beta} \\ & + \lambda_b^j \langle ib || aj \rangle^{\beta} \\ & - \lambda_b^i f_{ja}^{\beta} t_j^b \\ & - \lambda_a^j f_{ib}^{\beta} t_j^b \\ & + \lambda_c^j \langle ci || ba \rangle^{\beta} t_j^b \\ & - \lambda_c^i \langle cj || ba \rangle^{\beta} t_j^b \\ & - \lambda_b^k \langle ji || ka \rangle^{\beta} t_j^b \\ & + \lambda_a^k \langle ji || kb \rangle^{\beta} t_j^b \\ & + \lambda_b^j \langle ki || ca \rangle^{\beta} t_{jk}^{bc} \\ & + \frac{1}{2} \lambda_b^i \langle jk || ca \rangle^{\beta} t_{jk}^{bc} \\ & + \frac{1}{2} \lambda_a^j \langle ki || bc \rangle^{\beta} t_{jk}^{bc} \\ & - \lambda_c^j \langle ki || ba \rangle^{\beta} t_k^c t_j^b \\ & + \lambda_c^i \langle kj || ba \rangle^{\beta} t_k^c t_j^b \\ & + \lambda_a^k \langle ji || cb \rangle^{\beta} t_k^c t_j^b \\ & + \frac{1}{2} \lambda_{cd}^{ji} \langle cd || ba \rangle^{\beta} t_j^b \\ & + \frac{1}{2} \lambda_{ba}^{kl} \langle ji || kl \rangle^{\beta} t_j^b \\ & - \lambda_{cb}^{ki} \langle jc || ak \rangle^{\beta} t_j^b \\ & - \lambda_{ca}^{kj} \langle ic || bk \rangle^{\beta} t_j^b \\ & - \frac{1}{2} \lambda_{bc}^{ji} \langle bc || aj \rangle^{\beta} \end{aligned}$$

Table 17--continued

$$\begin{aligned}
& + \frac{1}{2} \lambda_{ba}^{jk} \langle ib || jk \rangle^{\beta} \\
& - \frac{1}{2} \lambda_{bc}^{ji} f_{ka}^{\beta} t_{jk}^{bc} \\
& - \frac{1}{2} \lambda_{ba}^{jk} f_{ic}^{\beta} t_{jk}^{bc} \\
& - \frac{1}{2} \lambda_{db}^{jk} \langle di || ca \rangle^{\beta} t_{jk}^{bc} \\
& + \lambda_{db}^{ji} \langle dk || ca \rangle^{\beta} t_{jk}^{bc} \\
& - \frac{1}{4} \lambda_{da}^{jk} \langle di || bc \rangle^{\beta} t_{jk}^{bc} \\
& + \frac{1}{2} \lambda_{bc}^{lj} \langle ki || la \rangle^{\beta} t_{jk}^{bc} \\
& + \frac{1}{4} \lambda_{bc}^{li} \langle jk || la \rangle^{\beta} t_{jk}^{bc} \\
& - \lambda_{ba}^{lj} \langle ki || lc \rangle^{\beta} t_{jk}^{bc} \\
& - \lambda_{dc}^{ji} \langle dk || ba \rangle^{\beta} t_k^c t_j^b \\
& - \frac{1}{2} \lambda_{da}^{kj} \langle di || cb \rangle^{\beta} t_k^c t_j^b \\
& + \frac{1}{2} \lambda_{cb}^{li} \langle kj || la \rangle^{\beta} t_k^c t_j^b \\
& + \lambda_{ca}^{lj} \langle ki || lb \rangle^{\beta} t_k^c t_j^b \\
& - \frac{1}{2} \lambda_{cd}^{kj} \langle li || ba \rangle^{\beta} t_{kl}^{cd} t_j^b \\
& + \frac{1}{2} \lambda_{cd}^{ki} \langle lj || ba \rangle^{\beta} t_{kl}^{cd} t_j^b \\
& + \frac{1}{4} \lambda_{cd}^{ji} \langle kl || ba \rangle^{\beta} t_{kl}^{cd} t_j^b \\
& - \frac{1}{2} \lambda_{cb}^{kl} \langle ji || da \rangle^{\beta} t_{kl}^{cd} t_j^b \\
& + \frac{1}{2} \lambda_{ca}^{kl} \langle ji || db \rangle^{\beta} t_{kl}^{cd} t_j^b \\
& - \lambda_{cb}^{ki} \langle lj || da \rangle^{\beta} t_{kl}^{cd} t_j^b \\
& - \lambda_{ca}^{kj} \langle li || db \rangle^{\beta} t_{kl}^{cd} t_j^b \\
& + \frac{1}{4} \lambda_{ba}^{kl} \langle ji || cd \rangle^{\beta} t_{kl}^{cd} t_j^b
\end{aligned}$$

Table 17--continued

$$\begin{aligned}
& + \frac{1}{2} \lambda_{dc}^{ji} \langle lk || ba \rangle^{\beta} t_1^d t_k^c t_j^b \\
& + \frac{1}{2} \lambda_{da}^{kj} \langle li || cb \rangle^{\beta} t_1^d t_k^c t_j^b \quad] \\
& + \tau_{ij}^{ab} \times [\quad \lambda_a^i f_{jb}^{\beta} \\
& \quad + \lambda_a^i \langle kj || cb \rangle^{\beta} t_k^c \\
& \quad + \frac{1}{2} \lambda_c^i \langle cj || ab \rangle^{\beta} \\
& \quad - \frac{1}{2} \lambda_a^k \langle ij || kb \rangle^{\beta} \\
& \quad - \frac{1}{2} \lambda_c^i \langle kj || ab \rangle^{\beta} t_k^c \\
& \quad - \frac{1}{2} \lambda_a^k \langle ij || cb \rangle^{\beta} t_k^c \\
& \quad + \frac{1}{2} \lambda_{ab}^{ki} f_{jk}^{\beta} \\
& \quad - \frac{1}{2} \lambda_{ca}^{ij} f_{cb}^{\beta} \\
& \quad + \frac{1}{8} \lambda_{cd}^{ij} \langle cd || ab \rangle^{\beta} \\
& \quad + \frac{1}{8} \lambda_{ab}^{kl} \langle ij || kl \rangle^{\beta} \\
& \quad + \lambda_{ca}^{ki} \langle jc || bk \rangle^{\beta} \\
& \quad + \frac{1}{2} \lambda_{ca}^{ij} f_{kb}^{\beta} t_k^c \\
& \quad + \frac{1}{2} \lambda_{ab}^{ki} f_{jc}^{\beta} t_k^c \\
& \quad - \frac{1}{4} \lambda_{dc}^{ij} \langle dk || ab \rangle^{\beta} t_k^c \\
& \quad + \lambda_{da}^{ki} \langle dj || cb \rangle^{\beta} t_k^c \\
& \quad + \frac{1}{2} \lambda_{da}^{ij} \langle dk || cb \rangle^{\beta} t_k^c \\
& \quad - \lambda_{ca}^{li} \langle kj || lb \rangle^{\beta} t_k^c \\
& \quad + \frac{1}{4} \lambda_{ab}^{lk} \langle ij || lc \rangle^{\beta} t_k^c \\
& \quad - \frac{1}{2} \lambda_{ab}^{li} \langle kj || lc \rangle^{\beta} t_k^c
\end{aligned}$$

Table 17--continued

$$\begin{aligned}
& - \frac{1}{4} \lambda_{cd}^{ki} \langle 1j || ab \rangle^\beta t_{kl}^{cd} \\
& + \frac{1}{16} \lambda_{cd}^{ij} \langle kl || ab \rangle^\beta t_{kl}^{cd} \\
& - \frac{1}{4} \lambda_{ca}^{kl} \langle ij || db \rangle^\beta t_{kl}^{cd} \\
& + \lambda_{ca}^{ki} \langle 1j || db \rangle^\beta t_{kl}^{cd} \\
& - \frac{1}{4} \lambda_{ca}^{ij} \langle kl || db \rangle^\beta t_{kl}^{cd} \\
& + \frac{1}{16} \lambda_{ab}^{kl} \langle ij || cd \rangle^\beta t_{kl}^{cd} \\
& - \frac{1}{4} \lambda_{ab}^{ki} \langle 1j || cd \rangle^\beta t_{kl}^{cd} \\
& + \frac{1}{8} \lambda_{dc}^{ij} \langle 1k || ab \rangle^\beta t_1^d t_k^c \\
& - \lambda_{da}^{ki} \langle 1j || cb \rangle^\beta t_1^d t_k^c \\
& - \frac{1}{2} \lambda_{da}^{ij} \langle 1k || cb \rangle^\beta t_1^d t_k^c \\
& + \frac{1}{8} \lambda_{ab}^{lk} \langle ij || dc \rangle^\beta t_1^d t_k^c \\
& - \frac{1}{2} \lambda_{ab}^{li} \langle kj || dc \rangle^\beta t_1^d t_k^c \\
& + \frac{1}{4} \lambda_{cda}^{kij} \langle cd || bk \rangle^\beta \\
& - \frac{1}{4} \lambda_{cab}^{kli} \langle jc || kl \rangle^\beta \quad] \\
& + \tau_{ijk}^{abc} \times \left[\frac{1}{4} \lambda_c^k \langle ij || ab \rangle^\beta \right. \\
& + \frac{1}{4} \lambda_{ab}^{ij} f_{kc}^\beta \\
& - \frac{1}{4} \lambda_{da}^{ij} \langle dk || bc \rangle^\beta \\
& + \frac{1}{4} \lambda_{ab}^{li} \langle jk || lc \rangle^\beta \\
& - \frac{1}{12} \lambda_{abc}^{lij} f_{kl}^\beta \\
& \left. + \frac{1}{12} \lambda_{dab}^{ijk} f_{dc}^\beta \right]
\end{aligned}$$

Note: Summation over all labels is implied.

The symbol τ represents derivative t-amplitudes; the derivative is with respect to α , evaluated at $\alpha=\beta=0$.

Table 18. Contributions to the Second Derivative of the CCSDT-1 Energy from:

$$\langle 0 | \Lambda ((H_N e^T)_c T^\alpha)_c T^\beta)_c | 0 \rangle.$$

$$\begin{aligned} \epsilon_i^a \times & \left[- \lambda_b^i f_{ja} \tau_j^b \right. \\ & - \lambda_a^j f_{ib} \tau_j^b \\ & + \lambda_c^j \langle ci || ba \rangle \tau_j^b \\ & - \lambda_c^i \langle cj || ba \rangle \tau_j^b \\ & - \lambda_b^k \langle ji || ka \rangle \tau_j^b \\ & + \lambda_a^k \langle ji || kb \rangle \tau_j^b \\ & + \lambda_b^j \langle ki || ca \rangle \tau_{jk}^{bc} \\ & + \frac{1}{2} \lambda_b^i \langle jk || ca \rangle \tau_{jk}^{bc} \\ & + \frac{1}{2} \lambda_a^j \langle ki || bc \rangle \tau_{jk}^{bc} \\ & - \lambda_c^j \langle ki || ba \rangle t_k^c \tau_j^b \\ & + \lambda_c^i \langle kj || ba \rangle t_k^c \tau_j^b \\ & + \lambda_a^k \langle ji || cb \rangle t_k^c \tau_j^b \\ & - \lambda_c^j \langle ki || ba \rangle t_j^b \tau_k^c \\ & + \lambda_c^i \langle kj || ba \rangle t_j^b \tau_k^c \\ & + \lambda_a^k \langle ji || cb \rangle t_j^b \tau_k^c \\ & + \frac{1}{2} \lambda_{cd}^{ji} \langle cd || ba \rangle \tau_j^b \\ & + \frac{1}{2} \lambda_{ba}^{kl} \langle ji || kl \rangle \tau_j^b \\ & - \lambda_{cb}^{ki} \langle jc || ak \rangle \tau_j^b \\ & - \lambda_{ca}^{kj} \langle ic || bk \rangle \tau_j^b \\ & - \frac{1}{2} \lambda_{bc}^{ji} f_{ka} \tau_{jk}^{bc} \end{aligned}$$

Table 18--continued

-	$\frac{1}{2}$	λ_{ba}^{jk}	f_{ic}	τ_{jk}^{bc}
-	$\frac{1}{2}$	λ_{db}^{jk}	$\langle di ca \rangle$	τ_{jk}^{bc}
+		λ_{db}^{ji}	$\langle dk ca \rangle$	τ_{jk}^{bc}
-	$\frac{1}{4}$	λ_{da}^{jk}	$\langle di bc \rangle$	τ_{jk}^{bc}
+	$\frac{1}{2}$	λ_{bc}^{lj}	$\langle ki la \rangle$	τ_{jk}^{bc}
+	$\frac{1}{4}$	λ_{bc}^{li}	$\langle jk la \rangle$	τ_{jk}^{bc}
-		λ_{ba}^{lj}	$\langle ki lc \rangle$	τ_{jk}^{bc}
-		λ_{dc}^{ji}	$\langle dk ba \rangle$	$t_k^c \tau_j^b$
-		λ_{da}^{kj}	$\langle di cb \rangle$	$t_k^c \tau_j^b$
+		λ_{cb}^{li}	$\langle kj la \rangle$	$t_k^c \tau_j^b$
+		λ_{ca}^{lj}	$\langle ki lb \rangle$	$t_k^c \tau_j^b$
-		λ_{dc}^{ji}	$\langle dk ba \rangle$	$t_j^b \tau_k^c$
+		λ_{ca}^{lj}	$\langle ki lb \rangle$	$t_j^b \tau_k^c$
-	$\frac{1}{2}$	λ_{cd}^{kj}	$\langle li ba \rangle$	$t_{kl}^{cd} \tau_j^b$
+	$\frac{1}{2}$	λ_{cd}^{ki}	$\langle lj ba \rangle$	$t_{kl}^{cd} \tau_j^b$
+	$\frac{1}{4}$	λ_{cd}^{ji}	$\langle kl ba \rangle$	$t_{kl}^{cd} \tau_j^b$
-	$\frac{1}{2}$	λ_{cb}^{kl}	$\langle ji da \rangle$	$t_{kl}^{cd} \tau_j^b$
+	$\frac{1}{2}$	λ_{ca}^{kl}	$\langle ji db \rangle$	$t_{kl}^{cd} \tau_j^b$
-		λ_{cb}^{ki}	$\langle lj da \rangle$	$t_{kl}^{cd} \tau_j^b$
-		λ_{ca}^{kj}	$\langle li db \rangle$	$t_{kl}^{cd} \tau_j^b$
+	$\frac{1}{4}$	λ_{ba}^{kl}	$\langle ji cd \rangle$	$t_{kl}^{cd} \tau_j^b$

Table 18--continued

$$\begin{aligned}
& - \frac{1}{2} \lambda_{cd}^{kj} \langle li || ba \rangle \tau_{kl}^{cd} t_j^b \\
& + \frac{1}{2} \lambda_{cd}^{ki} \langle lj || ba \rangle \tau_{kl}^{cd} t_j^b \\
& + \frac{1}{4} \lambda_{cd}^{ji} \langle kl || ba \rangle \tau_{kl}^{cd} t_j^b \\
& - \frac{1}{2} \lambda_{cb}^{kl} \langle ji || da \rangle \tau_{kl}^{cd} t_j^b \\
& + \frac{1}{2} \lambda_{ca}^{kl} \langle ji || db \rangle \tau_{kl}^{cd} t_j^b \\
& - \lambda_{cb}^{ki} \langle lj || da \rangle \tau_{kl}^{cd} t_j^b \\
& - \lambda_{ca}^{kj} \langle li || db \rangle \tau_{kl}^{cd} t_j^b \\
& + \frac{1}{4} \lambda_{ba}^{kl} \langle ji || cd \rangle \tau_{kl}^{cd} t_j^b \\
& + \frac{1}{2} \lambda_{dc}^{ji} \langle lk || ba \rangle t_1^d t_k^c t_j^b \\
& + \lambda_{da}^{kj} \langle li || cb \rangle t_1^d t_k^c t_j^b \\
& + \lambda_{dc}^{ji} \langle lk || ba \rangle t_1^d t_k^c t_j^b \\
& + \frac{1}{2} \lambda_{da}^{kj} \langle li || cb \rangle t_1^d t_k^c t_j^b \Big] \\
& + \epsilon_{ij}^{ab} \times \Big[\lambda_a^i \langle kj || cb \rangle \tau_k^c \\
& - \frac{1}{2} \lambda_c^i \langle kj || ab \rangle \tau_k^c \\
& - \frac{1}{2} \lambda_a^k \langle ij || cb \rangle \tau_k^c \\
& + \frac{1}{2} \lambda_{ca}^{ij} f_{kb} \tau_k^c \\
& + \frac{1}{2} \lambda_{ab}^{ki} f_{jc} \tau_k^c \\
& - \frac{1}{4} \lambda_{dc}^{ij} \langle dk || ab \rangle \tau_k^c \\
& + \lambda_{da}^{ki} \langle dj || cb \rangle \tau_k^c \\
& + \frac{1}{2} \lambda_{da}^{ij} \langle dk || cb \rangle \tau_k^c \\
& - \lambda_{ca}^{li} \langle kj || lb \rangle \tau_k^c
\end{aligned}$$

Table 18--continued

+	$\frac{1}{4}$	$\lambda_{ab}^{lk} \langle ij lc \rangle$	τ_k^c
-	$\frac{1}{2}$	$\lambda_{ab}^{li} \langle kj lc \rangle$	τ_k^c
-	$\frac{1}{4}$	$\lambda_{cd}^{ki} \langle lj ab \rangle$	τ_{kl}^{cd}
+	$\frac{1}{16}$	$\lambda_{cd}^{ij} \langle kl ab \rangle$	τ_{kl}^{cd}
-	$\frac{1}{4}$	$\lambda_{ca}^{kl} \langle ij db \rangle$	τ_{kl}^{cd}
+		$\lambda_{ca}^{ki} \langle lj db \rangle$	τ_{kl}^{cd}
-	$\frac{1}{4}$	$\lambda_{ca}^{ij} \langle kl db \rangle$	τ_{kl}^{cd}
+	$\frac{1}{16}$	$\lambda_{ab}^{kl} \langle ij cd \rangle$	τ_{kl}^{cd}
-	$\frac{1}{4}$	$\lambda_{ab}^{ki} \langle lj cd \rangle$	τ_{kl}^{cd}
+	$\frac{1}{4}$	$\lambda_{dc}^{ij} \langle lk ab \rangle$	$t_1^d \tau_k^c$
-		$\lambda_{da}^{ki} \langle lj cb \rangle$	$t_1^d \tau_k^c$
-		$\lambda_{da}^{ki} \langle lj cb \rangle$	$\tau_1^d \tau_k^c$
-	$\frac{1}{2}$	$\lambda_{da}^{ij} \langle lk cb \rangle$	$t_1^d \tau_k^c$
-	$\frac{1}{2}$	$\lambda_{da}^{ij} \langle lk cb \rangle$	$\tau_1^d \tau_k^c$
+	$\frac{1}{4}$	$\lambda_{ab}^{lk} \langle ij dc \rangle$	$t_1^d \tau_k^c$
-	$\frac{1}{2}$	$\lambda_{ab}^{li} \langle kj dc \rangle$	$t_1^d \tau_k^c$
-	$\frac{1}{2}$	$\lambda_{ab}^{li} \langle kj dc \rangle$	$\tau_1^d \tau_k^c]$

Note: Summation over all labels is implied.

The symbol τ represents derivative t-amplitudes; the derivative is with respect to α , evaluated at $\alpha=\beta=0$.

The symbol τ represents the derivative t-amplitudes where the derivative is with respect to β , evaluated at $\alpha=\beta=0$.

SCF orbitals $\{\phi(\alpha, \beta)\}$, expanded in a primitive AO basis set $\{\psi(\alpha, \beta)\}$ are now summarized.

We follow Handy et al.,²⁹ and choose non-canonical orbitals such that the second derivative of an orbital, evaluated at $\alpha=\beta=0$, is given by a linear combination of unperturbed SCF orbitals where there are no singularities arising from degeneracies among orbital eigenvalues. Of course, there are contributions from the second derivative of the primitive AO functions, as well.

$$|a^{\alpha\beta}\rangle = \sum_f U_{fa}^{\alpha\beta} |f\rangle + \sum_k U_{ka}^{\alpha\beta} |k\rangle + \sum_\mu C_{\mu a} |u^{\alpha\beta}\rangle$$

$$|i^{\alpha\beta}\rangle = \sum_f U_{fi}^{\alpha\beta} |f\rangle + \sum_k U_{ki}^{\alpha\beta} |k\rangle + \sum_\mu C_{\mu i} |u^{\alpha\beta}\rangle$$

where
$$U_{fa}^{\alpha\beta} = -\frac{1}{2} \xi_{fa}^{\alpha\beta} \quad \text{and} \quad U_{ki}^{\alpha\beta} = -\frac{1}{2} \xi_{ki}^{\alpha\beta}$$

The coefficients $U_{pq}^{\alpha\beta}$ are the second-order CPHF coefficients. The virtual-occupied block of the CPHF coefficients are determined by solving the second-order CPHF equation:^{30,40}

$$U_{ai}^{\alpha\beta} = \sum_{bj} (A^{-1})_{ai,bj} \frac{O_{bj}^{\alpha\beta}}{\epsilon_j - \epsilon_b},$$

where
$$A_{ai,bj} = 1 + \frac{\langle ab || ij \rangle + \langle aj || ib \rangle}{\epsilon_a - \epsilon_i}.$$

Note that the matrix A is the same as in the first-order CPHF equation given in Equation (21). The occupied-virtual second-order CPHF coefficients are determined by the second derivative of the SCF orthonormality condition:

$$U_{pq}^{\alpha\beta} + (U_{qp}^{\alpha\beta})^* + \xi_{pq}^{\alpha\beta} = 0,$$

where

$$\xi_{pq}^{\alpha\beta} = S_{pq}^{\alpha\beta} + \sum_r (U_{pr}^\alpha U_{qr}^\beta + U_{qr}^\alpha U_{pr}^\beta - S_{pr}^\alpha S_{qr}^\beta - S_{pr}^\beta S_{qr}^\alpha) .$$

The elements of the matrix $Q^{\alpha\beta}$ are given by:

$$\begin{aligned} Q_{pq}^{\alpha\beta} = & h_{pq}^{\alpha\beta} - S_{pq}^{\alpha\beta} \zeta_{pq} - \sum_{k,l} S_{kl}^{\alpha\beta} \langle pl || qk \rangle \\ & + \sum_{s,j} U_{sj}^\alpha \{ \langle ps || qj \rangle^\beta + \langle pj || qs \rangle^\beta \} \\ & + \sum_{s,j} U_{sj}^\beta \{ \langle ps || qj \rangle^\alpha + \langle pj || qs \rangle^\alpha \} \\ & + \sum_{s,t,j} U_{sj}^\alpha U_{tj}^\beta \{ \langle ps || qt \rangle + \langle pt || qs \rangle \} \\ & + \sum_s U_{sp}^\alpha f_{sq}^\beta + \sum_s U_{sq}^\alpha f_{ps}^\beta + \sum_s U_{sp}^\alpha f_{sq}^\beta + \sum_s U_{sq}^\beta f_{ps}^\alpha \\ & - \sum_s \left(U_{sp}^\alpha U_{qs}^\beta \epsilon_q + U_{sp}^\beta U_{qs}^\alpha \epsilon_q + U_{sq}^\alpha U_{ps}^\beta \epsilon_p \right. \\ & \quad \left. + U_{sq}^\beta U_{ps}^\alpha \epsilon_p + U_{sp}^\alpha U_{sq}^\beta \epsilon_s + U_{sp}^\beta U_{sq}^\alpha \epsilon_s \right) \\ & + \sum_{\substack{\mu, \nu \\ \lambda, \sigma}} (C_{\mu p})^* C_{\nu q} P_{\lambda \sigma} \left. \frac{\partial \langle \mu(\alpha, \beta) | h(\alpha, \beta) | \nu(\alpha, \beta) \rangle}{\partial \alpha \partial \beta} \right|_{\alpha=\beta=0} \end{aligned}$$

where

$$\zeta_{pq} = \begin{cases} \frac{1}{2} (\epsilon_p + \epsilon_q) & \text{when } p \text{ and } q \text{ are both} \\ & \text{virtual or occupied} \\ \epsilon_q & \text{otherwise} \end{cases} .$$

The matrix $h_{pq}^{\alpha\beta}$ consists of the derivative of the matrix elements of the one-electron part of the Hamiltonian in the primitive, perturbation-dependent basis $\{\mu(\alpha, \beta)\}$, but transformed into the unperturbed orbital basis $\{\phi\}$.

$$h_{pq}^{\alpha\beta} = \sum_{\mu, \nu} (C_{\mu p})^* C_{\nu q} \left. \frac{\partial \langle \mu(\alpha, \beta) | h(\alpha, \beta) | \nu(\alpha, \beta) \rangle}{\partial \alpha \partial \beta} \right|_{\alpha=\beta=0}$$

Similarly, the matrix $S_{pq}^{\alpha\beta}$ is the derivative of the overlap matrix of the perturbation-dependent primitive basis functions, transformed into

the unperturbed orbital basis.

$$S_{pq}^{\alpha\beta} = \sum_{\mu, \nu} (C_{\mu p})^* C_{\nu q} \left. \frac{\partial \langle \mu(\alpha, \beta) | \nu(\alpha, \beta) \rangle}{\partial \alpha \partial \beta} \right|_{\alpha=\beta=0}$$

For the choice of non-canonical orbitals, the off-diagonal elements $f_{ab}^{\alpha\beta}$ and $f_{ij}^{\alpha\beta}$ are not zero. These matrix elements are given by:

$$f_{ab}^{\alpha\beta} = Q_{ab}^{\alpha\beta} + \sum_{g,m} U_{gm}^{\alpha\beta} (\langle am || bg \rangle + \langle ag || bm \rangle)$$

$$f_{ij}^{\alpha\beta} = Q_{ij}^{\alpha\beta} + \sum_{g,m} U_{gm}^{\alpha\beta} (\langle im || jg \rangle + \langle ig || jm \rangle) .$$

Recall that the third and seventh terms of Equation (40) are analogous to the first derivative of the energy presented in Table (1). Now, using the identities from CPHF theory, we may expand the derivative integrals just as in the previous section. We will obtain, in analogy with the first derivative, the following:

$$\begin{aligned} \Delta E^{\alpha\beta} = & \sum_{i,j} D_{ij} Q_{ij}^{\alpha\beta} + \sum_{a,b} D_{ab} Q_{ab}^{\alpha\beta} + 2 \sum_{a,i} D_{ai} Q_{ai}^{\alpha\beta} \quad (41) \\ & + \sum_{i,j} I_{ij} \xi_{ij}^{\alpha\beta} + \sum_{a,b} I_{ab} \xi_{ab}^{\alpha\beta} + 2 \sum_{a,i} I_{ai} \xi_{ai}^{\alpha\beta} \\ & + \text{AO/AO, AO/MO and MO/MO derivative parts} \\ & + \frac{1}{4} \sum_{\substack{i,j, \\ a,b}} \langle ab || ij \rangle^{\alpha} \tau_{ij}^{ab} + \sum_{\substack{i,j, \\ a,b}} \langle ab || ij \rangle^{\alpha} \tau_i^a \tau_j^b \\ & + \frac{1}{4} \sum_{\substack{i,j, \\ a,b}} \langle ab || ij \rangle^{\beta} \tau_{ij}^{ab} + \sum_{\substack{i,j, \\ a,b}} \langle ab || ij \rangle^{\beta} \tau_i^a \tau_j^b \\ & + \sum_{\substack{i,j, \\ a,b}} \langle ab || ij \rangle \tau_i^a \tau_j^b \\ & + \text{Terms 5,6 and 8 of Equation (40)} . \end{aligned}$$

The intermediate I and the density matrix D are exactly as defined in the previous section. The A0/A0, A0/M0 and M0/M0 derivative parts, not explicitly shown above, are presented in Table (19). Recall that terms 5, 6 and 8 of Equation (40) are summarized in Tables (17) and (18) and that the derivative t -amplitudes are determined by solving the coupled, linear equations given in Tables (14-16). Of course, the matrix elements f_{ai} , f_{ia} , f_{ai}^α and f_{ia}^α are zero for the choice of SCF basis functions, wherever they may occur in the tables. The matrix elements f_{ab}^α and f_{ij}^α are given in Equations (30) and (31). Finally, the derivative integrals which appear in Equation (41) are dependent upon the first-order CPHF coefficients. The derivative of a general integral $\langle pq||rs \rangle$ is given by:

$$\langle pq||rs \rangle^\alpha =$$

$$\sum_{\mu, \nu, \rho, \sigma} (C_{\rho r} C_{\sigma s} - C_{\rho s} C_{\sigma r}) C_{\mu p}^* C_{\nu q}^* \frac{\partial \langle \mu(\alpha, \beta) \nu(\alpha, \beta) | \rho(\alpha, \beta) \sigma(\alpha, \beta) \rangle}{\partial \alpha} \bigg|_{\alpha=\beta=0}$$

$$+ \sum_t \left[\langle tq||rs \rangle U_{tp}^\alpha + \langle pt||rs \rangle U_{tq}^\alpha + \langle pq||ts \rangle U_{tr}^\alpha + \langle pq||rt \rangle U_{ts}^\alpha \right].$$

MBPT Second Derivatives

Now we extract the finite-order MBPT second derivatives from Equation (41). Inspection of the first six terms of Equation (41) reveals that, as with the first derivative, the second derivative of

the n^{th} -order correlation energy depends upon the n^{th} -order MBPT density matrix D and the n^{th} -order intermediate I . The finite-order MBPT densities and I intermediates are discussed in the previous section; Tables (9-12) prescribe the Γ intermediates necessary for their construction. The appropriate n^{th} -order AO/AO, AO/MO and MO/MO derivative parts of Equation (41) are obtained by evaluating the contributions given in Table (19) using the Γ intermediates so defined. The appropriate n^{th} -order contributions from the remaining terms in Equation (41) are obtained in a straightforward fashion by using various low-order iterates of the unperturbed t -amplitudes, the λ -amplitudes and the derivative t -amplitudes. We summarize these remaining contributions for the MBPT(2), MBPT(3), MBPT(4) and D-MBPT(∞) models in Tables (20) through (23), respectively. The low-order iterates of the derivative t -amplitudes are summarized in Table (24).

Table 19. The AO/AO, AO/MO and MO/MO Derivative Parts of the Second Derivative of the CC/MBPT Energy.

$$\text{AO/AO derivative part} = \sum_{\mu, \nu, \rho, \sigma} \langle \mu(\alpha, \beta) \nu(\alpha, \beta) | \rho(\alpha, \beta) \sigma(\alpha, \beta) \rangle^{\alpha\beta} \Gamma(\mu\nu\rho\sigma)$$

$$\begin{aligned} \text{AO/MO and MO/MO derivative parts} = & \sum_{\substack{i,j, \\ a,b}} \Gamma(ij,ab) \langle ij||ab \rangle^{(\alpha\beta)} + \sum_{\substack{a,b, \\ c,d}} \Gamma(ab,cd) \langle ab||cd \rangle^{(\alpha\beta)} \\ & + \sum_{\substack{i,j, \\ k,l}} \Gamma(ij,kl) \langle ij||kl \rangle^{(\alpha\beta)} + \sum_{\substack{j,a, \\ b,i}} \Gamma(ja,bi) \langle ja||bi \rangle^{(\alpha\beta)} \\ & + \sum_{\substack{i,a, \\ j,b}} \Gamma(ja,bi) \langle ja||bi \rangle^{(\alpha\beta)} + \sum_{\substack{i,a, \\ b,c}} \Gamma(ai,bc) \langle ai||bc \rangle^{(\alpha\beta)} \\ & + \sum_{\substack{i,a, \\ j,k}} \Gamma(jk,ia) \langle jk||ia \rangle^{(\alpha\beta)} \end{aligned}$$

where we define

$$\begin{aligned} \langle pq||rs \rangle^{(\alpha\beta)} = & \sum_{\mu, \nu, \rho, \sigma} \langle \mu(\alpha, \beta) \nu(\alpha, \beta) | \rho(\alpha, \beta) \sigma(\alpha, \beta) \rangle^{\alpha} \left((C_{\rho r} C_{\sigma s} - C_{\rho s} C_{\sigma r}) C_{\mu t} C_{\nu q} U_{tp}^{\beta} \right. \\ & + (C_{\rho r} C_{\sigma s} - C_{\rho s} C_{\sigma r}) C_{\mu p} C_{\nu t} U_{tq}^{\beta} \\ & + (C_{\rho t} C_{\sigma s} - C_{\rho s} C_{\sigma t}) C_{\mu p} C_{\nu q} U_{tr}^{\beta} \\ & \left. + (C_{\rho r} C_{\sigma t} - C_{\rho t} C_{\sigma r}) C_{\mu p} C_{\nu q} U_{ts}^{\beta} \right) \\ & + \sum_{t,u} \left(\langle tu||rs \rangle U_{tp}^{\alpha} U_{uq}^{\beta} + \langle tq||us \rangle U_{tp}^{\alpha} U_{ur}^{\beta} + \langle tq||ru \rangle U_{tp}^{\alpha} U_{us}^{\beta} \right. \\ & \left. + \langle pt||us \rangle U_{tq}^{\alpha} U_{ur}^{\beta} + \langle pt||ru \rangle U_{tq}^{\alpha} U_{us}^{\beta} + \langle pq||tu \rangle U_{tr}^{\alpha} U_{us}^{\beta} \right) \\ & + \text{all of the above with } \alpha \leftrightarrow \beta \end{aligned}$$

Note: The $\langle \mu\nu|\rho\sigma \rangle^{\alpha\beta}$ denotes the second derivative of an ordinary AO two-electron integral, evaluated at $\alpha=\beta=0$. $\langle \mu\nu|\rho\sigma \rangle^{\alpha}$ is the derivative with respect to α , evaluated at $\alpha=\beta=0$. $\Gamma(\mu\nu\rho\sigma)$ is defined in Table (7).

See Table (6) for the definitions of the Γ intermediates. The CPHF coefficients U_{pq}^{α} are given in Equations (28,29).

Table 20. Remaining Contributions to the MBPT(2) Second Derivative.

$$\begin{aligned}
& \frac{1}{4} \langle ab || ij \rangle^{\alpha} \tau_{ij}^{ab}(1) + \frac{1}{4} \langle ab || ij \rangle^{\beta} \tau_{ij}^{ab}(1) \\
& + \frac{1}{2} \tau_{ki}^{ab}(1) f_{jk}^{\beta} \tau_{ij}^{ab}(1) + \frac{1}{2} \tau_{ki}^{ab}(1) f_{jk}^{\alpha} \tau_{ij}^{ab}(1) \\
& - \frac{1}{2} \tau_{ij}^{ca}(1) f_{cb}^{\beta} \tau_{ij}^{ab}(1) - \frac{1}{2} \tau_{ij}^{ca}(1) f_{cb}^{\alpha} \tau_{ij}^{ab}(1)
\end{aligned}$$

Note: Summation over all labels is implied.

Table 21. Remaining Contributions to the MBPT(3) Second Derivative.

$$\begin{aligned}
& \frac{1}{4} \langle ab || ij \rangle^\alpha \tau_{ij}^{ab}(2) + \frac{1}{4} \langle ab || ij \rangle^\beta \tau_{ij}^{ab}(2) \\
& + \frac{1}{2} \Delta t_{ki}^{ab}(2) f_{jk}^\beta \tau_{ij}^{ab}(1) + \frac{1}{2} \Delta t_{ki}^{ab}(2) f_{jk}^\alpha \tau_{ij}^{ab}(1) \\
& + \frac{1}{2} \tau_{ki}^{ab}(1) f_{jk}^\beta \Delta t_{ij}^{ab}(2) + \frac{1}{2} \tau_{ki}^{ab}(1) f_{jk}^\alpha \Delta t_{ij}^{ab}(2) \\
& - \frac{1}{2} \Delta t_{ij}^{ca}(2) f_{cb}^\beta \tau_{ij}^{ab}(1) - \frac{1}{2} \Delta t_{ij}^{ca}(2) f_{cb}^\alpha \tau_{ij}^{ab}(1) \\
& - \frac{1}{2} \tau_{ij}^{ca}(1) f_{cb}^\beta \Delta t_{ij}^{ab}(2) - \frac{1}{2} \tau_{ij}^{ca}(1) f_{cb}^\alpha \Delta t_{ij}^{ab}(2) \\
& + \frac{1}{8} \tau_{ij}^{cd}(1) \langle cd || ab \rangle^\beta \tau_{ij}^{ab}(1) + \frac{1}{8} \tau_{ij}^{cd}(1) \langle cd || ab \rangle^\alpha \tau_{ij}^{ab}(1) \\
& + \frac{1}{8} \tau_{kl}^{ab}(1) \langle ij || kl \rangle^\beta \tau_{ij}^{ab}(1) + \frac{1}{8} \tau_{kl}^{ab}(1) \langle ij || kl \rangle^\alpha \tau_{ij}^{ab}(1) \\
& + \tau_{ki}^{ca}(1) \langle jc || bk \rangle^\beta \tau_{ij}^{ab}(1) + \tau_{ki}^{ca}(1) \langle jc || bk \rangle^\alpha \tau_{ij}^{ab}(1)
\end{aligned}$$

Note: Summation over all labels is implied.

Table 22. Remaining Contributions to the MBPT(4) Second Derivative.

$$\begin{aligned}
& \frac{1}{4} \langle ab || ij \rangle^\alpha \tau_{ij}^{ab}(3) + \frac{1}{4} \langle ab || ij \rangle^\beta \tau_{ij}^{ab}(3) \\
& + \frac{1}{8} \Delta t_{ij}^{cd}(2) \langle cd || ab \rangle^\beta \tau_{ij}^{ab}(1) + \frac{1}{8} \Delta t_{ij}^{cd}(2) \langle cd || ab \rangle^\alpha \tau_{ij}^{ab}(1) \\
& + \frac{1}{8} t_{ij}^{cd}(1) \langle cd || ab \rangle^\beta \Delta \tau_{ij}^{ab}(2) + \frac{1}{8} t_{ij}^{cd}(1) \langle cd || ab \rangle^\alpha \Delta \tau_{ij}^{ab}(2) \\
& + \frac{1}{8} \Delta t_{kl}^{ab}(2) \langle ij || kl \rangle^\beta \tau_{ij}^{ab}(1) + \frac{1}{8} \Delta t_{kl}^{ab}(2) \langle ij || kl \rangle^\alpha \tau_{ij}^{ab}(1) \\
& + \frac{1}{8} t_{kl}^{ab}(1) \langle ij || kl \rangle^\beta \Delta \tau_{ij}^{ab}(2) + \frac{1}{8} t_{kl}^{ab}(1) \langle ij || kl \rangle^\alpha \Delta \tau_{ij}^{ab}(2) \\
& + \Delta t_{ki}^{ca}(2) \langle jc || bk \rangle^\beta \tau_{ij}^{ab}(1) + \Delta t_{ki}^{ca}(2) \langle jc || bk \rangle^\alpha \tau_{ij}^{ab}(1) \\
& + t_{ki}^{ca}(1) \langle jc || bk \rangle^\beta \Delta \tau_{ij}^{ab}(2) + t_{ki}^{ca}(1) \langle jc || bk \rangle^\alpha \Delta \tau_{ij}^{ab}(2) \\
& + \frac{1}{4} t_{ij}^{ab}(1) Q_{ij}^{ab}(I, \tau(1) \times \epsilon(1)) + \frac{1}{4} t_{ij}^{ab}(1) Q_{ij}^{ab}(I, \epsilon(1) \times \tau(1)) \\
& + \frac{1}{4} t_{ij}^{ab}(1) Q_{ij}^{ab}(I^\beta, t(1) \times \tau(1)) + \frac{1}{4} t_{ij}^{ab}(1) Q_{ij}^{ab}(I^\beta, \tau(1) \times t(1)) \\
& + \frac{1}{4} t_{ij}^{ab}(1) Q_{ij}^{ab}(I^\alpha, t(1) \times \epsilon(1)) + \frac{1}{4} t_{ij}^{ab}(1) Q_{ij}^{ab}(I^\alpha, \epsilon(1) \times t(1)) \\
& + t_i^b(2) f_{ba}^\beta \tau_i^a(2) + t_i^b(2) f_{ba}^\alpha \tau_i^a(2) \\
& - t_j^a(2) f_{ij}^\beta \tau_i^a(2) - t_j^a(2) f_{ij}^\alpha \tau_i^a(2) \\
& - \frac{1}{2} t_{ji}^{bc}(1) \langle bc || aj \rangle^\beta \tau_i^a(2) - \frac{1}{2} t_{ji}^{bc}(1) \langle bc || aj \rangle^\alpha \tau_i^a(2) \\
& + \frac{1}{2} t_{jk}^{ba}(1) \langle ib || jk \rangle^\beta \tau_i^a(2) + \frac{1}{2} t_{jk}^{ba}(1) \langle ib || jk \rangle^\alpha \tau_i^a(2) \\
& + \frac{1}{2} t_i^c(2) \langle cj || ab \rangle^\beta \tau_{ij}^{ab}(1) + \frac{1}{2} t_i^c(2) \langle cj || ab \rangle^\alpha \tau_{ij}^{ab}(1) \\
& - \frac{1}{2} t_k^a(2) \langle ij || kb \rangle^\beta \tau_{ij}^{ab}(1) - \frac{1}{2} t_k^a(2) \langle ij || kb \rangle^\alpha \tau_{ij}^{ab}(1) \\
& + \frac{1}{4} t_{kij}^{cda}(2) \langle cd || bk \rangle^\beta \tau_{ij}^{ab}(1) + \frac{1}{4} t_{kij}^{cda}(2) \langle cd || bk \rangle^\alpha \tau_{ij}^{ab}(1) \\
& - \frac{1}{4} t_{kli}^{cab}(2) \langle jc || kl \rangle^\beta \tau_{ij}^{ab}(1) - \frac{1}{4} t_{kli}^{cab}(2) \langle jc || kl \rangle^\alpha \tau_{ij}^{ab}(1) \\
& - \frac{1}{4} t_{ij}^{da}(1) \langle dk || bc \rangle^\beta \tau_{ijk}^{abc}(2) - \frac{1}{4} t_{ij}^{da}(1) \langle dk || bc \rangle^\alpha \tau_{ijk}^{abc}(2) \\
& + \frac{1}{4} t_{li}^{ab}(1) \langle jk || lc \rangle^\beta \tau_{ijk}^{abc}(2) + \frac{1}{4} t_{li}^{ab}(1) \langle jk || lc \rangle^\alpha \tau_{ijk}^{abc}(2) \\
& - \frac{1}{12} t_{lij}^{abc}(2) f_{kl}^\beta \tau_{ijk}^{abc}(2) - \frac{1}{12} t_{lij}^{abc}(2) f_{kl}^\alpha \tau_{ijk}^{abc}(2)
\end{aligned}$$

Table 22--continued

$$+ \frac{1}{12} t_{ijk}^{dab}(2) f_{dc}^{\beta} \tau_{ijk}^{abc}(2) \quad + \frac{1}{12} t_{ijk}^{dab}(2) f_{dc}^{\alpha} \tau_{ijk}^{abc}(2)$$

Note: Summation over all labels is implied.

Table 23. Remaining Contributions to the LCCD or (D-MBPT(∞)) Second Derivative.

$$\begin{aligned}
 & \frac{1}{4} \langle ab || ij \rangle^\alpha \epsilon_{ij}^{ab}(\infty) + \frac{1}{4} \langle ab || ij \rangle^\beta \tau_{ij}^{ab}(\infty) \\
 & + \frac{1}{2} t_{ki}^{ab}(\infty) f_{jk}^\beta \tau_{ij}^{ab}(\infty) + \frac{1}{2} t_{ki}^{ab}(\infty) f_{jk}^\alpha \epsilon_{ij}^{ab}(\infty) \\
 & - \frac{1}{2} t_{ij}^{ca}(\infty) f_{cb}^\beta \tau_{ij}^{ab}(\infty) - \frac{1}{2} t_{ij}^{ca}(\infty) f_{cb}^\alpha \epsilon_{ij}^{ab}(\infty) \\
 & + \frac{1}{8} t_{ij}^{cd}(\infty) \langle cd || ab \rangle^\beta \tau_{ij}^{ab}(\infty) + \frac{1}{8} t_{ij}^{cd}(\infty) \langle cd || ab \rangle^\alpha \epsilon_{ij}^{ab}(\infty) \\
 & + \frac{1}{8} t_{kl}^{ab}(\infty) \langle ij || kl \rangle^\beta \tau_{ij}^{ab}(\infty) + \frac{1}{8} t_{kl}^{ab}(\infty) \langle ij || kl \rangle^\alpha \epsilon_{ij}^{ab}(\infty) \\
 & + t_{ki}^{ca}(\infty) \langle jc || bk \rangle^\beta \tau_{ij}^{ab}(\infty) + t_{ki}^{ca}(\infty) \langle jc || bk \rangle^\alpha \epsilon_{ij}^{ab}(\infty)
 \end{aligned}$$

Note: Summation over all labels is implied.

The symbol $\tau_{ij}^{ab}(\infty)$ represents the converged LCCD derivative t-amplitudes.

Table 24. The Low-order Iterates of T^α .

$$\tau_{ij}^{ab}(1) = \langle ij || ab \rangle^\alpha / D_{ij}^{ab}$$

$$\tau_{ij}^{ab}(2) = \tau_{ij}^{ab}(1) + \Delta\tau_{ij}^{ab}(2)$$

$$\begin{aligned} \Delta\tau_{ij}^{ab}(2) = & \left[\frac{1}{2} \tau_{ij}^{cd}(1) \langle ab || cd \rangle + \frac{1}{2} \tau_{kl}^{ab}(1) \langle ij || kl \rangle \right. \\ & + P(ab|ij) \tau_{ki}^{ca}(1) \langle jc || bk \rangle \\ & + \frac{1}{2} \tau_{ij}^{cd}(1) \langle ab || cd \rangle^\alpha + \frac{1}{2} \tau_{kl}^{ab}(1) \langle ij || kl \rangle^\alpha \\ & \left. + P(ab|ij) \tau_{ki}^{ca}(1) \langle jc || bk \rangle^\alpha \right] / D_{ij}^{ab} \end{aligned}$$

$$\tau_{ij}^{ab}(3) = \tau_{ij}^{ab}(1) + \Delta\tau_{ij}^{ab}(2) + \Delta\tau_{ij}^{ab}(3; \text{SDT}) + \Delta\tau_{ij}^{ab}(3; 0)$$

$$\begin{aligned} \Delta\tau_{ij}^{ab}(3; 0) = & \{ Q_{ij}^{ab}(I, t(1) \times \tau(1)) + Q_{ij}^{ab}(I, \tau(1) \times t(1)) \\ & + Q_{ij}^{ab}(I^\alpha, t(1) \times t(1)) \} / D_{ij}^{ab} \end{aligned}$$

$$\begin{aligned} \Delta\tau_{ij}^{ab}(3; \text{SDT}) = & \left[\frac{1}{2} \Delta\tau_{ij}^{cd}(2) \langle ab || cd \rangle + \frac{1}{2} \Delta\tau_{kl}^{ab}(2) \langle ij || kl \rangle \right. \\ & + P(ab|ij) \Delta\tau_{ki}^{ca}(2) \langle jc || bk \rangle \\ & + \frac{1}{2} \Delta\tau_{ij}^{cd}(2) \langle ab || cd \rangle^\alpha + \frac{1}{2} \Delta\tau_{kl}^{ab}(2) \langle ij || kl \rangle^\alpha \\ & + P(ab|ij) \Delta\tau_{ki}^{ca}(2) \langle jc || bk \rangle^\alpha \\ & + P(ij) \tau_i^c(2) \langle cj || ab \rangle - P(ab) \tau_k^a(2) \langle ij || kb \rangle \\ & + P(ij) \tau_i^c(2) \langle cj || ab \rangle^\alpha - P(ab) \tau_k^a(2) \langle ij || kb \rangle^\alpha \\ & + \frac{1}{2} P(ab) \tau_{kij}^{cda}(2) \langle cd || bk \rangle - \frac{1}{2} P(ab) \tau_{kli}^{cab}(2) \langle jc || kl \rangle \\ & \left. + \frac{1}{2} P(ab) \tau_{kij}^{cda}(2) \langle cd || bk \rangle^\alpha - \frac{1}{2} P(ab) \tau_{kli}^{cab}(2) \langle jc || kl \rangle^\alpha \right] / D_{ij}^{ab} \end{aligned}$$

Table 24--continued

$$\tau_i^a(2) = \left[-\frac{1}{2} \tau_{ji}^{bc}(1) \langle bc||aj \rangle + \frac{1}{2} \tau_{jk}^{ba}(1) \langle ib||jk \rangle - \frac{1}{2} \tau_{ji}^{bc}(1) \langle bc||aj \rangle^\alpha + \frac{1}{2} \tau_{jk}^{ba}(1) \langle ib||jk \rangle^\alpha \right] / D_i^a$$

$$\begin{aligned} \tau_{ijk}^{abc}(2) = & \left[-P(a/bc|k/ij) \tau_{ij}^{da}(1) \langle dk||bc \rangle \right. \\ & + P(c/ab|i/jk) \tau_{11}^{ab}(1) \langle jk||lc \rangle \\ & - P(a/bc|k/ij) \tau_{ij}^{da}(1) \langle dk||bc \rangle^\alpha \\ & \left. + P(c/ab|i/jk) \tau_{11}^{ab}(1) \langle jk||lc \rangle^\alpha \right] / D_{ijk}^{abc} \end{aligned}$$

Note: Summation over all labels is implied.

The symbol τ represents the derivative t -amplitudes, where the derivative is with respect to α , evaluated at $\alpha=\beta=0$.

$P(*)$ refers to various operators which generate terms with permuted labels. See the notes in Tables (3) and (4) for the definitions of such operators.

See Table (13) for the low-order iterates of T and definitions of other related quantities.

CONCLUSION

The theory of analytic CC and MBPT first and second derivatives has been presented; an efficient strategy has been described for the evaluation of molecular gradients and first-order one-electron response properties. The expressions for the first derivative of the CCSDT energy--including the CCSDT response density--have been made explicit. The expressions for the second derivative of the CCSDT-1 energy have been presented in terms of the response density and derivative t-amplitudes. The theory of first and second derivatives of the MBPT models through fourth order has been extracted as a special case of the theory of CC derivatives.

A report of several analytic response properties of water computed through the SDQ-MBPT(4) level of theory and using a large Gaussian basis set has been accepted for publication. We have published a report of the application of MBPT(3) gradients to small closed-shell molecular systems using basis sets of limited size.⁴¹ In the report, we presented the theory of MBPT(2) and MBPT(3) response densities for the first time and included values of MBPT(2) and MBPT(3) dipole moments as examples of analytic property evaluation.

One-electron response properties through the SDQ-MBPT(4) level of theory and for the LCCD model are currently possible. Molecular gradients are available through the D-MBPT(4) model and for the LCCD model. It is possible to obtain plots of the MBPT response density, as well; a recent study of the dissociation of methane includes a

series of MBPT density plots at various C-H bondlengths. All implementation has been general; that is, applicable to the case of UHF orbitals as well as RHF orbitals. Naturally, the UHF-MBPT response density is now being used in spin-density studies. Current progress is being made to extend gradient/property evaluation to the full MBPT(4) model and the CCD model.

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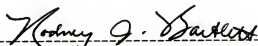
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BIOGRAPHICAL SKETCH

Edward Alan Salter was born March 18, 1961, in Mobile, Alabama, where his parents, Dr. and Mrs. Otha C. Salter, reside. He has two older brothers, Otha Carlisle, Jr. and David Christian, both now married, and one younger sister, Susanna Julia. Mr. Salter attended Spring Hill College in Mobile; he graduated with honors in May of 1981, receiving a Bachelor of Science degree in chemistry. Born into a family of professionals, he had little choice but to pursue some form of graduate-level education. The "lost decade," or "era of graduate studies," began in August, 1982.

As he is an Alabama fan, Mr. Salter has necessarily followed college football all his life. He has a general interest in the sciences. Of those who know him, none doubts that he loves cats or drinks Coca-Cola or that he enjoys watching television and movies. Some place him on the conservative end of the political spectrum. As for the possibility of doing post-doctoral research, Mr. Salter occasionally suggests that he "would rather lose [his] left _____."

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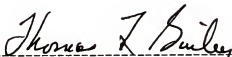
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N. Yngve Örn
Professor of Chemistry and Physics

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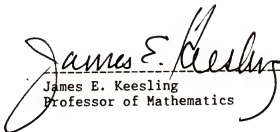
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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August, 1988

Dean, Graduate School